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Volume 1. Measurement Studies and Combustion Sources, September 15-16, 1987
Boulder, Colorado

Energy and Environmental Research Corp.
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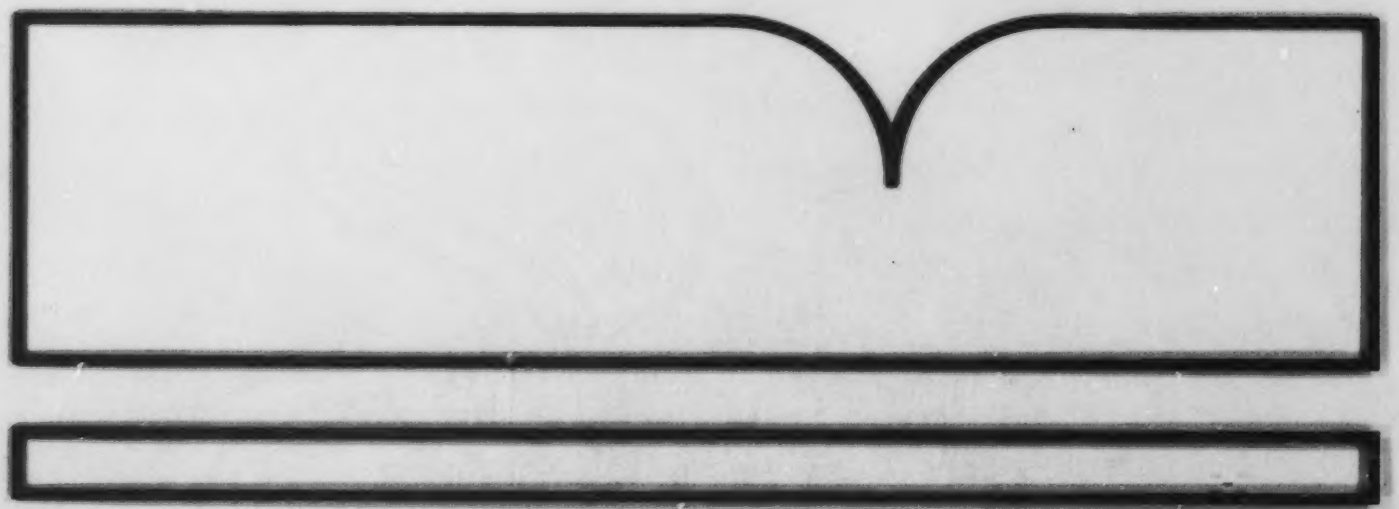

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16. ABSTRACT

The report documents activities during a portion of the second workshop on atmospheric nitrous oxide (N2O) at Boulder, Colorado, on September 15-16, 1987. (The first was held February 13-14, 1986, at Durham, North Carolina.) Among workshop goals were: to provide an opportunity for a more timely exchange of information among researchers than would otherwise be possible through normal technical channels; to prioritize the research that is needed to determine if atmospheric N2O is a problem; and to understand the importance of various sources and sinks. The technical discussion involved three areas: (1) measurement approaches, (2) combustion sources of N2O, and (3) biogenic sources of N2O. Within each area, the focus was on using the best current understanding to develop the research priorities needed to assess the severity of the N2O problem. This volume focuses on the first two areas; Volume II is to focus on the third.

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Volume I: Measurement Studies and Combustion Sources

September 15-16, 1987

Boulder, Colorado

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ABSTRACT

On September 15-16, 1987, the U.S. Environmental Protection Agency, the National Oceanic and Atmospheric Administration, the National Aeronautics and Space Administration, and the Department of Agriculture jointly sponsored a workshop on atmospheric nitrous oxide (N_2O) at Boulder, Colorado. This meeting follows a previous workshop which was held at Durham, North Carolina, on February 13-14, 1986. These meetings served a number of purposes. One important objective was to provide an opportunity for a more timely exchange of information among researchers than would otherwise be possible through normal technical channels. Another major purpose was to prioritize the research that is needed to determine whether atmospheric N_2O is a problem, and to understand the importance of the various sources and sinks.

The technical discussion was focused into three areas:

1. Measurement approaches.
2. Combustion sources of N_2O.
3. Biogenic sources of N_2O.

Within each area, the focus was on using the best current understanding to develop the research priorities needed to assess the severity of the N_2O problem. This volume concerns the first two areas. The biogenic discussion is contained in Volume II.

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1.0 INTRODUCTION

This report summarizes a workshop on the atmospheric emission of nitrous oxide (N_2O) which was held at Boulder, Colorado, on September 15-16, 1987, under the joint sponsorship of the U.S. Environmental Protection Agency (EPA), the National Oceanographic and Atmospheric Administration (NOAA), the U.S. Department of Agriculture (USDA) and the National Aeronautics and Space Administration (NASA). Organizational responsibilities for this meeting were assumed by EPA's Air and Energy Engineering Research Laboratory with support from Energy and Environmental Research Corporation (EER). This was the second such workshop, the previous workshop having been held in Durham, North Carolina, February 13-14, 1986, under EPA sponsorship. The initial workshop was summarized by Lanier and Robinson (1986).

These two workshops were held as part of EPA's effort to develop an appropriate research plan with respect to N_2O. The atmospheric concentration of nitrous oxide is increasing steadily at a rate of approximately 0.25 percent per year. This is a matter of concern since nitrous oxide is one of several trace gases which cause ozone depletion and which contribute to the greenhouse effect. Depletion of the ozone layer will cause increasing amounts of solar UV radiation to reach the Earth's surface and result in increasing incidence of melanoma and other health problems. There is also concern about adverse ecological effects associated with increased UV-B radiation, e.g. decreased plankton in the oceans. Since the lifetime of N_2O in the atmosphere is more than a century, by the time such adverse health effects became acute it would be too late for any useful action. Similarly, the greenhouse effect to which N_2O contributes has the potential for causing significant climate changes.

While there are thus substantial reasons for concern, many aspects of the N_2O problem are poorly understood. There are important scientific questions which need to be answered before any rational decision regarding action is possible. Answering these questions requires developing a coherent research plan; this workshop was a step in formulating such a plan. The approach was to bring together a group of appropriate experts and allow them

to exchange information and develop a consensus as to which aspects of the N_2O problem are truly critical.

While there is presently no coordinated overall federal government plan for N_2O research and funding for N_2O research has been minimal, nonetheless a remarkable amount of progress has been made recently. Many aspects of the N_2O problem which were controversial or completely undefined are now generally agreed to, as will be discussed in the body of this report. Other aspects, also to be discussed, have emerged as exceedingly important unknowns in urgent need of greater understanding.

The organization of this report corresponds to the way in which the workshop was organized. The first session of the meeting was a set of overview presentations by representatives of the EPA, NASA, and NOAA which described their agencies' concerns regarding the effects of N_2O on the environment and what their agencies are doing with regard to these concerns. This portion of the meting is summarized herewith in the Environmental Concerns section. The second section of the meeting also dealt with a matter of importance to all attendees, the accurate measurements of N_2O, summarized herewith in the N_2O measurement section.

It is to be remembered that most of the scientists attending the meeting belonged to one of two rather different groups; i.e., one group consisted of physical scientists, engineers, and others with specialties relating to combustion and high-temperature chemical kinetics; the second group was primarily ecologists, agricultural and soil scientists, and atmospheric chemists. After the two general interest sessions, the meeting split into two smaller sections, so that each group of specialists could hold free-flowing informal discussions, these discussions being summarized herewith in the Biogenic Sources of N_2O and the Combustion Sources of N_2 sections. Each of these discussion sections involved both the formal presentations of research results and their implications. While the formal presentations are much more readily summarized, the most productive part of the meeting was clearly the unstructured discussions; this report will attempt to capture the spirit and substance of those discussions to the maximum extent possible.

clearly the unstructured discussions; this report will attempt to capture the spirit and substance of those discussions to the maximum extent possible.

2.0 ENVIRONMENTAL CONCERNS

The question of what increasing levels of N_2O mean to Planet Earth and its inhabitants was addressed by three speakers, Mr. Dennis Tirpak of EPA, Dr. Joel Levine of NASA, and Dr. Jim Elkins of NOAA, each of whom gave overviews of their agencies' programs in this area.

2.1 Overview of EPA Concerns

Mr. Tirpak's (EPA's Office of Planning and Evaluation) presentation was an overview of EPA's risk assessment studies of possible global climate change and the potential contribution of N_2O to this process. Two major studies by EPA have been requested by Congress, one dealing with the potential health and environmental effects of climate change and one dealing with the policy options for stabilizing the atmosphere.

These and other studies are being done within EPA with a complex conceptual framework shown schematically in Figure 1 (see Appendix A). The inputs to this framework, the left-most block, consists of a set of assumptions regarding human activity, how much energy we use, what our agricultural practices are, what control technologies we use, etc. From these assumptions the second block of the model calculates the emissions to the atmosphere of N_2O, CO_2, CH_4, chlorofluorocarbons, etc. from anthropogenic sources and the natural sources and sinks of these gases. The net inputs to the atmosphere are put to a chemical kinetics model of the complex chemistry which occurs in the atmosphere.

The Atmospheric Chemistry model in turn supplies input to an atmospheric temperature model which in turn feeds back to the emissions forecast model and the process repeats until convergence is achieved.

This complex model is necessary, Mr. Tirpak explained, because the behavior of the atmosphere is complex, filled with subtleties that one would not intuitively expect. For example, one major mechanism for the destruction of stratospheric ozone is a catalytic cycle involving NO and NO_2, $NO + O_3 =$

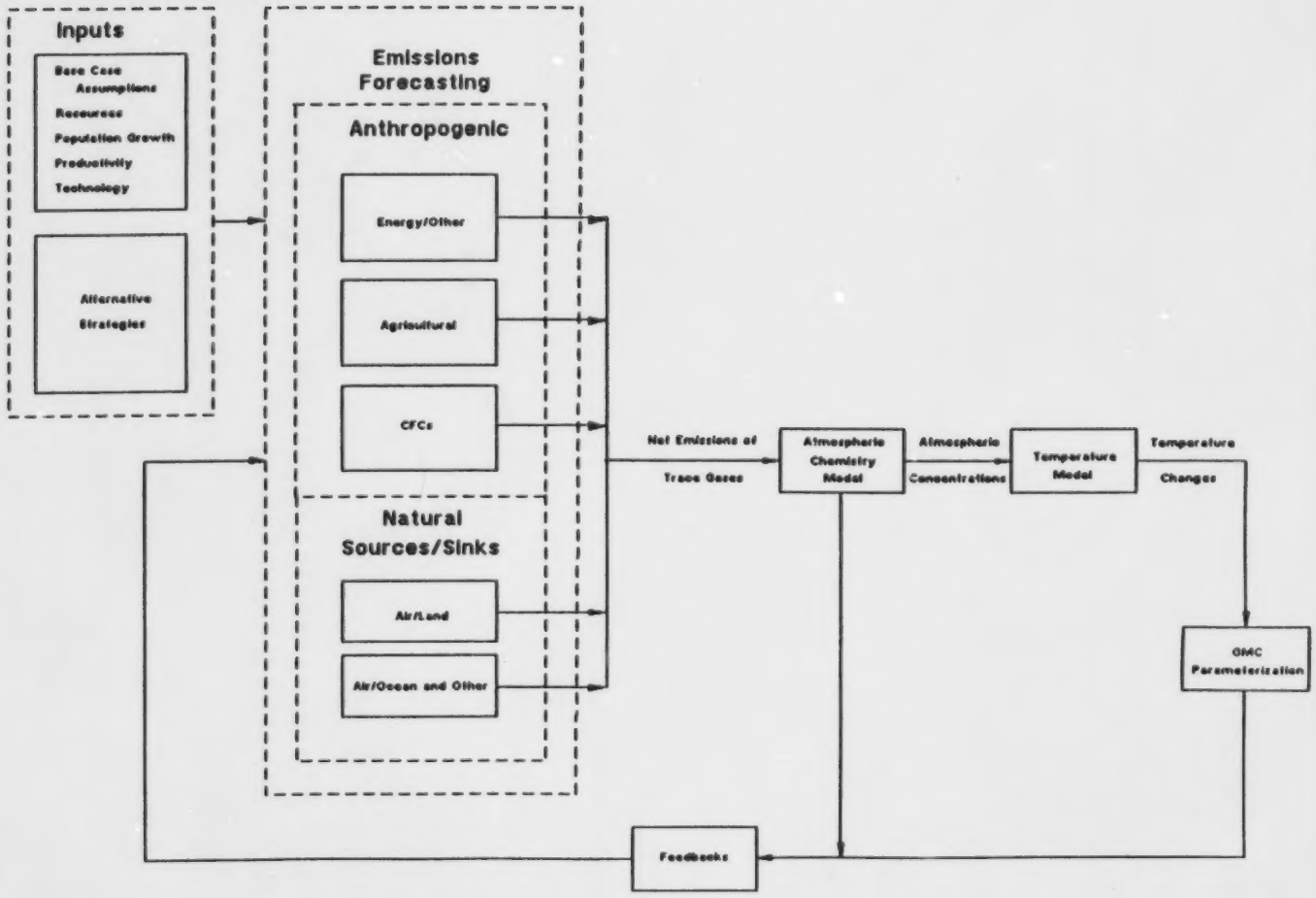


Figure 1. EPA model for atmospheric behavior forecasts.

NO2 + O2, $NO_2 + O_3 = NO + 2O_2$. One might therefore conclude that the release of NO_x ($NO + NO_2$) by processes such as coal combustion would be harmful to the ozone layer but such is not the case. NO_x is reactive, its lifetime in the troposphere too short for it to diffuse from the troposphere to the statosphere where the ozone layer is found. Along with the NO_x, however, N_2O is also released. Being much more inert it can diffuse to the stratosphere, where it can react with $O(^1D)$ atoms (i.e. oxygen atoms in an excited state) produced by the photolysis of ozone. This reaction, $N_2O + O(^1D) = 2NO$, produces the NO involved in the ozone destruction cycle described above.

The matter is further complicated, however, by the fact that chlorofluorocarbons are also released to the troposphere. Being inert they also can diffuse to the stratosphere where they decompose to yield Cl atoms. These then also serve as ozone decomposition catalysts via $Cl + O_3 = ClO + O_2$, $ClO + O = Cl + O_2$. Thus both NO_x and Cl are ozone decomposition catalysts but their effects are not additive because the reaction $ClO + NO_2 = ClONO_2$ can convert chain carriers in the two catalytic cycles to an inert form. As a result of this interaction, increasing ozone decomposition via the NO_x cycle (by increasing N_2O input) decreases ozone decomposition via the chlorine chain cycle. The converse is also true. Situations are thus possible in which increasing the input of an ozone destroying substance can lead to a net increase in the amount of ozone surviving.

This complex chemistry is further complicated by considerations of atmospheric temperature and heat balance. By absorbing ultraviolet light ozone provides an important mechanism of heat input to the stratosphere. The heat balance of the stratosphere, however, is also effected by all of the greenhouse gases. All of the chemistry discussed above is temperature dependent. As a result, as shown in Table 1, increasing carbon dioxide, which is chemically inert in the stratosphere, can add ozone.

After discussing the atmospheric modeling Mr. Tirpak presented data on the global sources and sinks of N_2O, Table 2, on the breakdown of the natural

TABLE 1. DEPENDENCE OF GLOBAL TEMPERATURE AND STRATOSPHERIC OZONE ON TRACE GASES, INCLUDING SYNERGISTIC EFFECTS

Compounds	*Stratospheric Ozone*	*Global Temperature*
Chlorofluorocarbons	**Depletes**	**Increases**
Halons (Bromine)	**Depletes**	**Increases**
Methane (CH_4)	**Counters Depletion: Adds Ozone (Troposphere)**	**Increases**
Nitrous Oxide (N_2O)	**Counters Depletion in High Chlorine Cases**	**Increases**
Carbon Dioxide (CO_2)	**Adds Ozone**	**Increases**

TABLE 2. GLOBAL SOURCES AND SINKS OF NITROUS OXIDE (N_2O)
(10^6 TONS AS N)

Atmospheric Burden	1500
Sinks	
Stratospheric photolysis + reaction with $O(^1D)$	10.5 +- 3
Sources (10^6 tons N per year)	
1. Natural	9.7
Tropical soil emissions	7.4 +- 4
Non-tropical soil emissions	0.1 +-0.5
Oceans	2.0 +- 1
Lightning	<0.1
2. Anthropogenic	5.5 +-8.4
Combustion	
Utility coal and oil	2.12
Industry coal and oil	1.64
Households coal and oil	0.24
Tropical biomass	0.6
Non-tropical biomass	0.1
Fertilized agricultural lands	0.6-2.3
Gain of cultivated land	0.2-0.6

Source: Table is adapted from McElroy and Wofsy, as reported in World Meteorological Organization. Atmospheric Ozone 1985: Assessment of our understanding of the processes controlling its present distribution and change. World Meteorological Organization, Geneva, Switzerland, 1986. Combustion emissions are computed based on 1975 source estimates presented in Kavanaugh, M., Estimates of future CO, N_2O and NO_x emissions from energy combustion. Atmospheric Environment. 21(3): 463-468, 1987."Lightning, Fertilizer and Cultivated Land". source from Seiler as reported in Scope 29 titled The Greenhouse Effect. Climatic Change and Ecosystems. 1987.

emissions for individual ecosystems, Table 3, and on the projected emissions by sector and region, Figure 2.

The major conclusion of Mr. Tirpak's talk is shown in Table 4. All studies show that if present trends are allowed to continue unchecked there will be a significant increase in mean global temperature.

2.2 Overview of NASA's Concerns

Dr. Joel Levine's presentations described NASA's program for measuring the composition of Earth's atmosphere from space. He showed dramatic pictures of the hole in the ozone layer over the South Pole; i.e., photos in which different concentrations of ozone were represented by different colors. Unfortunately, these dramatic photos cannot be satisfactorily reproduced in this black and white report.

The major point Dr. Levine made with respect to the photos was the ozone hole represented a major phenomenon which had not been predicted by any of the atmospheric chemistry models and which even in retrospect could not, to date, be explained by any of them. This failure of theory clearly showed the absolute need of using advanced methods to observe what was actually happening in the atmosphere.

Dr. Levine also discussed the current thinking on ozone chemistry in the stratosphere. In the natural O_3 formation and destruction cycle, NO_x (from N_2O) dominates in the lower stratosphere and HO_x is more dominant in the upper stratosphere. A key point is that approximately 70 percent of the natural O_3 destruction is due to stratospheric NO which in turn arises from natural N_2O emissions to the troposphere. Thus, increased N_2O emissions will eventually increase the absolute O_3 destruction rate, if the synergistic effects noted by Mr. Tirpak are not considered. The important conclusion is that natural N_2O already dominates stratospheric O_3 destruction, and thus increased N_2O emissions can be expected to directly translate into increased O_3 consumption.

TABLE 3. SUMMARY OF N_2O EMISSION RATES FROM INDIVIDUAL ECOSYSTEMS (IN T_g PER YEAR) THE LAST COLUMN PRESENTS NEW ESTIMATES FOR THIS VOLUME (W. SEILER).

Source	Hahn and Junge (1977)	Khahil and Rasmussen (1983b)	Crutzen (1983)	Seiler
Ocean/Freshwater	16-185	9.0	1-2	2
Natural soils	6-65	13.4	(?)	6
Fertilizer	6-20	--	<3	0.6-2.3
Gain of cultivated	--	6.6	1-3	0.2-0.6
Fossil fuel burning	1-4	--	1.8	--
Biomass burning	--	--	1-2	1-2
Lightning	10-55	--	--	<0.1
Total	80-300[a]	29	8-12	12-15

(a) includes N_2O production fom unknown sources

Source: As reported by Seiler in Scope 29: The Greenhouse Effect, Climatic Change, and Ecosystems.

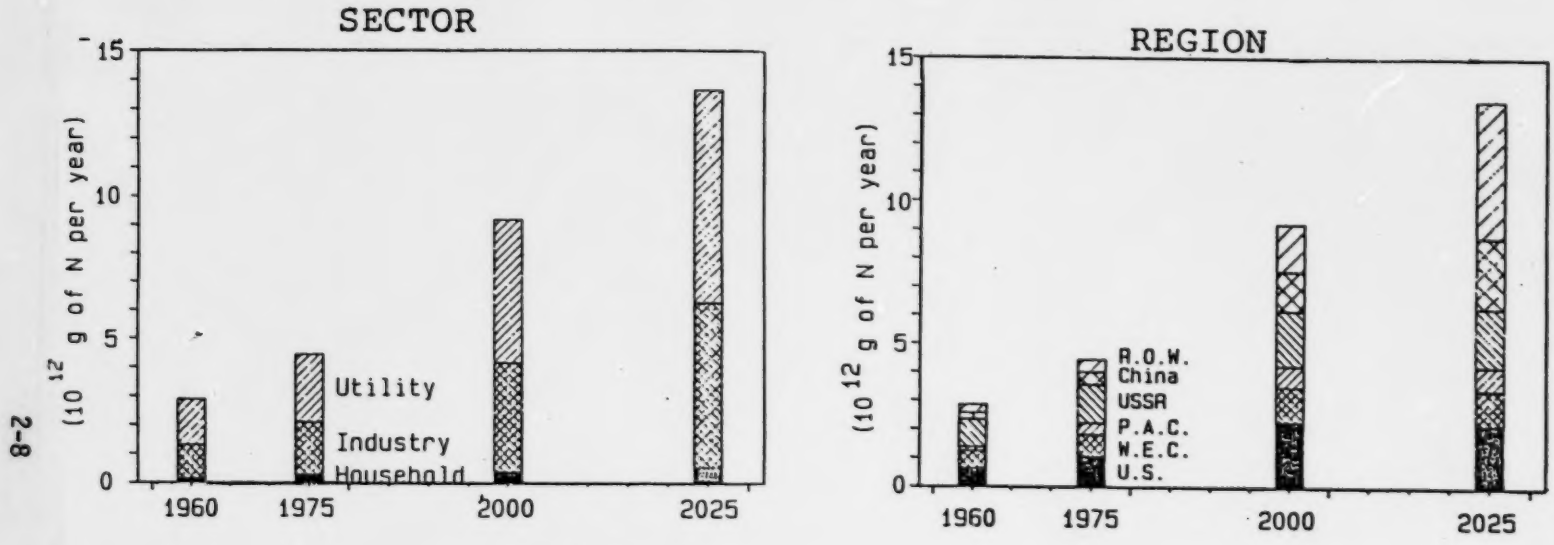


Figure 2. Historical and projected nitrous oxide (N_2O) emissions from combustion by sector and region. Increases in N_2O are large: a doubling in emissions from 1975 to 2000 and a 44 percent increase from 2000 to 2025. Source: Kavanaugh, M. Estimates of future CO, N_2O and NO_x emissions from energy combustion. Atmospheric Environment. 21(3): 463-468, 1987.

TABLE 4. ALL MAJOR ASSESSMENTS CONCLUDE THAT SUBSTANTIAL GLOBAL WARMING WILL OCCUR

- NAS 1979 -- "WE ESTIMATE THE MOST PROBABLE GLOBAL WARMING FOR A DOUBLING OF CO_2 TO BE NEAR 3°C WITH A PROBABLE ERROR OF ±1.5°C

  WE HAVE TRIED BUT HAVE BEEN UNABLE TO FIND ANY OVERLOOKED OR UNDERESTIMATED PHYSICAL EFFECT THAT COULD REDUCE THE CURRENTLY ESTIMATED GLOBAL WARMING TO NEGLIGIBLE PROPORTIONS. IT APPEARS THAT THE WARMING WILL EVENTUALLY OCCUR..."

- NAS 1982 -- "THE PRESENT STUDY HAS NOT FOUND ANY NEW RESULTS THAT NECESSITATE SUBSTANTIAL REVISION OF THE CONCLUSIONS OF THE (1979) REPORT."

- NAS 1983 -- "FROM CLIMATE MODEL SIMULATIONS OF INCREASED CO_2 WE CONCLUDE WITH CONSIDERABLE CONFIDENCE THAT THERE WOULD BE A GLOBAL MEAN TEMPERATURE INCREASE."

- VILLACH (UNEP, WMO, ICSU) 1985 -- "IF PRESENT TRENDS CONTINUE, THE COMBINED CONCENTRATIONS OF ATMOSPHERIC CO_2 AND OTHER GREENHOUSE GASES WOULD BE EQUIVALENT TO A DOUBLING OF CO_2 FROM PRE-INDUSTRIAL LEVELS BY POSSIBLY AS EARLY AS THE 2030s.

  ... THE GREENHOUSE GASES ARE LIKELY TO BE THE MOST IMPORTANT CAUSE OF CLIMATE CHANGE OVER THE NEXT CENTURY.

Dr. Levine next addressed the fate of stratospheric N_2O. According to the best current understanding, the following reactions account for the indicated percentage of N_2O destruction in the stratosphere

	(photolysis)		
N_2O	$\longrightarrow$	$N_2 + O(^1D)$	90%
$N_2O + O(^1D)$	$\longrightarrow$	2 NO	5%
$N_2O + O(^1D)$	$\longrightarrow$	$N_2 + O_2$	5%

Thus, only a fraction of the N_2O becomes NO, but this fraction is still responsible for 70 percent of the O_3 destruction in the baseline (natural) ozone balance.

In the rest of his talk Dr. Levine discussed a variety of spectroscopic methods of measuring atmospheric composition which NASA has developed. The material in this portion of Dr. Levine's presentation has been presented in detail in a publication which he edited, NASA Conference Publication 2450, "Space Opportunities for Tropospheric Chemistry Research," to which the reader is referred (Levine, 1987).

2.3 Overview of NOAA's Concerns

Dr. Jim Elkin's presentation in this session concerned NOAA's ongoing program of measuring the ambient N_2O concentration. The locations of the NOAA stations involved in this program are shown in Table 5. Table 6 shows the measured rates of increase of N_2O of 0.68 +/- 0.20 ppb yr^{-1} may be calculated. These results, and those of others leave no doubt that the tropospheric N_2O concentration is increasing, and that the rate of increase is of the order of 0.25%/year. This strongly suggests an important anthropogenic source flux.

TABLE 5. LOCATIONS OF NOAA/GMCC N_2O SAMPLING SITES AND PERIODS OF RECORD

Station	Latitude	Longitude	Elevation (m)	Sampling Period
Pt. Barrow, Alaska	71.21°N	130.60°W	12	8/77-8/84
Niwot Ridge, Colorado	40.05°N	105.64°W	3749	6/77-8/84
Mauna Loa, Hawaii	19.53°N	155.58°W	2297	6/77-8/84
American Samoa, South Pacific	14.25°S	170.56°W	82	6/77-8/84
South Pole, Antarctica	89.98°S	24.80°W	2810	1/77-8/84

TABLE 6. LEAST SQUARES REGRESSION STATISTICS FOR N_2O DATA

Station	Number of Observations	January 1, 1978 Concentration, ppbv	Growth Rate* ppbv yr^{-1},	Residual Standard Deviation, ppbv	Multiple Correlation Coefficient Squared
Barrow	326	301.16 ± 0.56	0.46 ± 0.07	1.224	0.369
Niwot Ridge	327	300.67 ± 0.70	0.76 ± 0.08	1.533	0.510
Mauna Loa	332	300.08 ± 0.66	0.71 ± 0.08	1.430	0.499
Samoa	313	298.93 ± 0.65	0.91 ± 0.09	1.649	0.554
South Pole	126	299.85 ± 1.30	0.60 ± 0.16	1.572	0.296

* Indicated uncertainties are 95% confidence interval standard errors.

3.0 MEASUREMENT OF N_2O

In any program involved in environmental measurements one is concerned with the accurate measurement of materials present in trace quantities and correspondingly the quality of measurements is always a concern. For N_2O this concern involves both short-term and long-term problems. In the short term there is the question of how highly skilled research scientists and their assistants can measure N_2O with satisfactory accuracy using procedures which are not unduly expensive or laborious. In the long term, however, it is clear that any program for limiting N_2O emissions will necessarily involve routinely measuring N_2O emissions, these measurements being done by far less skilled people and the acceptable levels of labor and cost being significantly reduced. The portion of the meeting which dealt with the measurement of N_2O involved both these aspects and included presentations by Dr. Jim Elkins of NOAA, Ms. Tami Montgomery of University of California at Irvine, and Dr. Mark Zahniser of Aerodyne.

3.1 N_2O Measurement by GC/ECD

Dr. Elkins discussed the G. C. Methods which were used in the ambient monitoring program he had previously described. Details of these experimental techniques are covered in a paper by W. D. Komkyr, T. M. Thompson and E. G. Dutton (Journal of Geophysical Research, in press). In most regards the GC techniques used by these workers are effectively equivalent to those discussed by Dr. Weiss at the previous workshop, e.g. while Dr. Weiss recommends the use of a 5A molecular sieve column at 240 C with an electron capture detector, the NOAA workers choose to use Porasil A at 175 C with an electron capture detector. The choice of carrier gas, however, represents a critical difference. The NOAA workers ran their GC with an N_2 carrier and a substantial portion of Dr. Elkins presentation concerned the painstaking measures which are necessary to account for the interference of CO_2 in the determination of N_2O. Such precautions were, in Dr. Elkin's view, necessary because of the mechanism by which an electron capture detector measures N_2O. The initial step in this mechanism is the capture of a low energy electron by N_2O: $N_2O + e^- = N_2 + O^-$. The O^- ion thus

formed can react further, $O^- + N_2O = NO^- + NO$, $NO^- + M = NO + e^- + M$. Since this reaction sequence causes the captured electron to be released, it decreases the amount of signal which the electron capture detector produces for a given amount of N_2O. If, however, CO_2 is present the reaction $CO_2 + O^- + M = CO_3^- + M$ can also occur, in competition with NO^- formation, increasing the sensitivity of the electron capture detector and making it necessary to correct any measurement of N_2O to take into account the amount of CO_2 present in the sample.

In comments from the floor Dr. Paul Golden made the point that this problem was merely one of many difficulties which arise in attempting to use N_2 carrier gas for an electron capture detector. N_2 is basically unsuitable for electron capture detectors, because the sensitivity of the detector is dependent on trace impurities, especially O_2, in the carrier gas. Use of truly pure N_2 as carrier causes the sensitivity of the electron capture detector to go to zero. This problem, however, does not seem to arise if one uses an Ar-CH_4 mixture as the carrier gas as was recommended by Dr. Weiss. Another aspect of the Weiss approach was the use of the Molecular Sieve column. On this column N_2O is eluted before CO_2, and therefore the interference is avoided. The one precaution is to allow sufficient time for the CO_2 peak to fully elute before starting the next analysis. This prevents an interference between the N_2O peak and the tail of the CO_2 peak from the preceding analysis.

During his discussion of the determination of N_2O with N_2 carrier, Dr. Elkins described a procedure for checking for interference by CO_2, one measured the N_2O content of the sample before and after passage through ascarite. Since ascarite removes CO_2 but has no effect on N_2O, any change in the measured N_2O concentration could reasonably be taken as CO_2 interference. While CO_2 interference does not appear to be a problem with the GC determination of N_2O with Ar-CH_4 carrier, still it was the sense of the meeting that this check for CO_2 interference is readily done and may be a generally useful precaution.

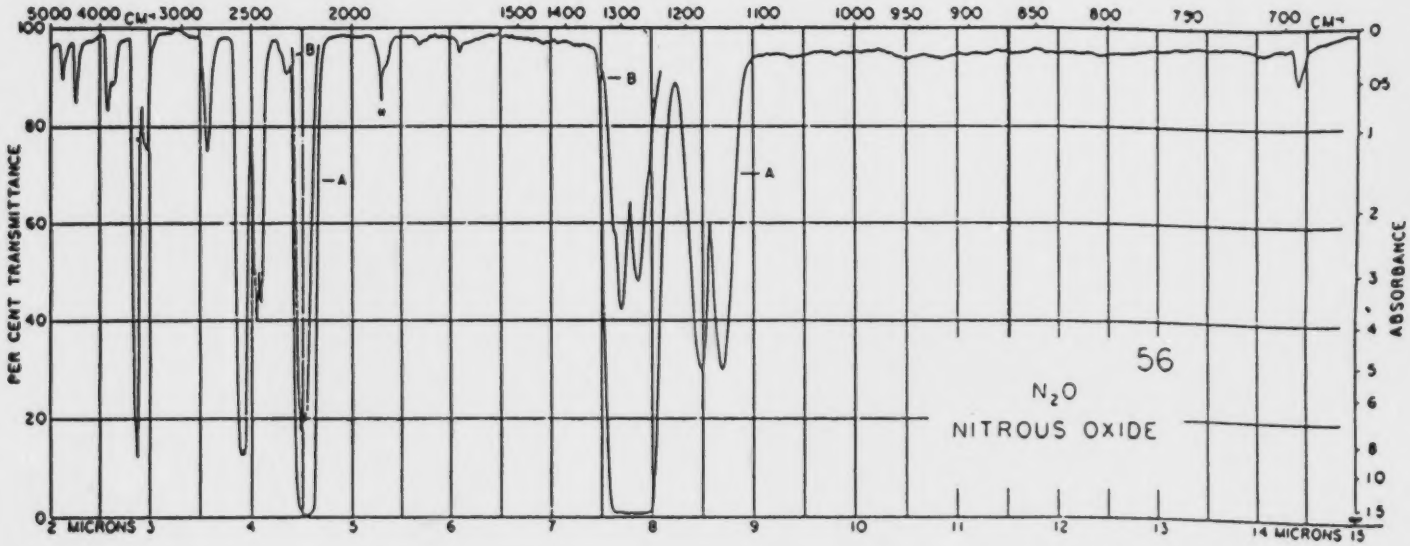
3.2 N_2O Measurement by IR Absorption

The next presentation was given by Ms. Tami Montgomery of the University of California, Irvine (UCI) and coauthored by Dr. L. J. Muzio of Fossil Energy Research and Prof. G. S. Samuelsen of UCI and described a project sponsored by the Electric Power Research Institute (EPRI). The objective of this project was to develop a continuous IR instrument for N_2O, suitable for routine monitoring of combustion processes.

The infrared spectrum of N_2O, shown in Figure 3, has strong absorption bands at 4.5 and 7.8 microns, either of which could be used for N_2O determination in a single wave-length analyzer in the absence of interfering gases. Combustion gases, however, contain a number of infrared active gases, CO, CO_2, NO, NO_2 and SO_2, which can also absorb radiation at these wavelengths. Figure 4 shows the experimental setup used in this project. The approach was to evaluate the interference of various gases by performing absorption measurements on well-characterized gas mixtures. A second element of the approach was to use scrubbers to selectively remove certain objectionable gas components. Table 7 shows typical experimental results.

Based on these results the authors feel they have achieved their initial goal; i.e., they have a method capable of accurately measuring N_2O at high concentrations. The problem of interference by NO_2 and SO_2 at 7.8 microns was resolved by scrubbing the sample gas with Na_2SO_3 and/or Na_2CO_3 solutions. The hardware necessary for this method consists of a single wavelength infrared device and a scrubbing system and is sufficiently simple and inexpensive to be suitable for use in source monitoring. The method in its present state of development will have an error in the range of 3-7 ppm N_2O. In some source monitoring situations the N_2O level would be high enough for such an error to be acceptable. In others it would not.

One suggestion which emerged from the workshop was that the principal remaining interference is from NO and that the authors might therefore use a scrubbing solution of NaOCl, which can remove NO as well as NO_2 and SO_2.



Curve letter		A	B
Pressure, mm.	No. 56	701	69
Resolution		927	900

* Absorbance at about 5.3 μ probably due to NO.

Figure 3. Infrared spectrum for N_2O.

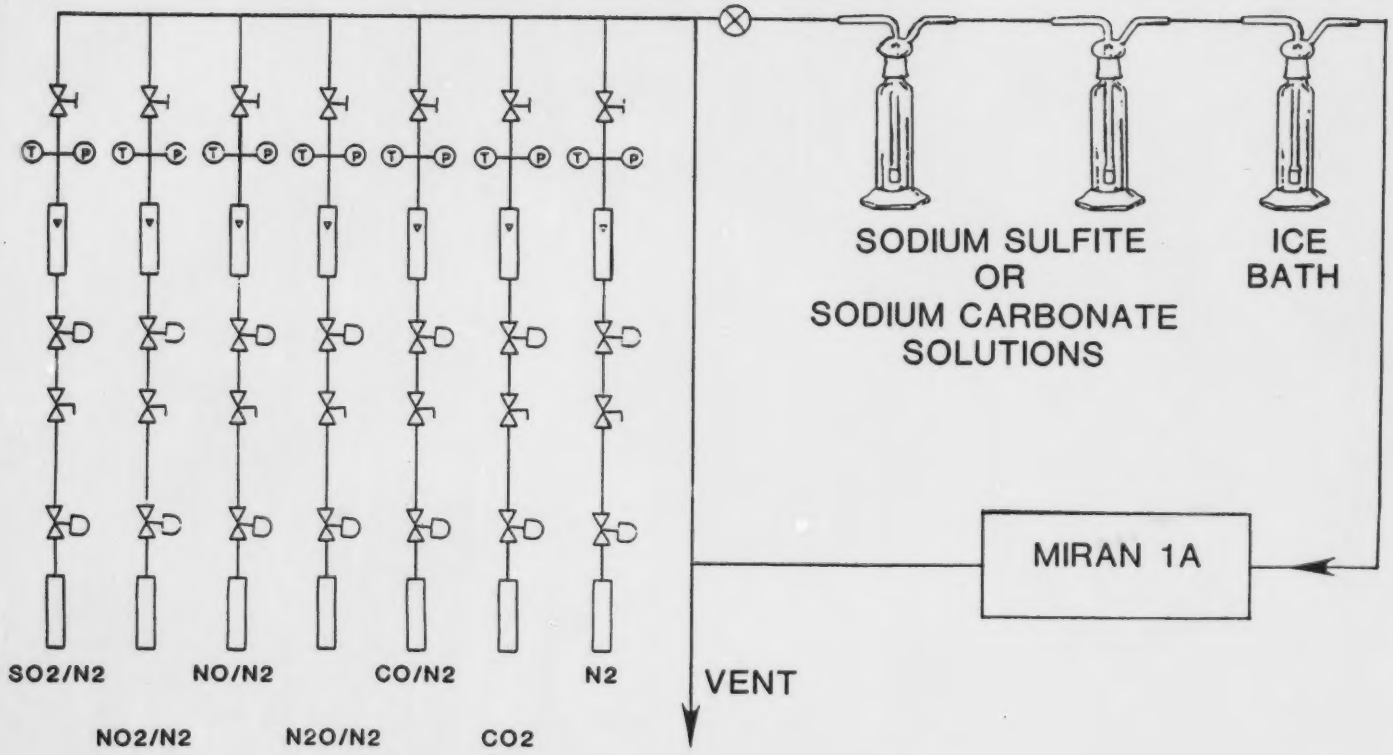


Figure 4. Experimental configuration used to evaluate N_2O measurement by IR absorption.

TABLE 7. RESULTS OF INTERFERENCE TESTS FOR N_2O MEASUREMENT BY IR ABSORPTION

NITROUS OXIDE INTERFERENCES

	SPECIES	CONCENTRATION	INTERFERENCES, PPM N_2O	
			λ=4.5 μ	λ=7.8 μ
a: low SO_2, low NO_X	CO_2	16 %	18.5	1.2
	CO	30 PPM	3.6	0.1
	NO_2	15 PPM	0.0	2.5
	NO	350 PPM	1.8	2.0
	SO_2	800 PPM	0.1	2.2
	N_2O	175 PPM	175	175
		TOTAL	199	183
	without scrubbing	% ERROR	13.7%	4.6%
	with scrubbing	% ERROR	13.6%	1.9%
b: high SO_2, high NO_X	CO_2	16 %	18.5	1.2
	CO	100 PPM	16.9	0.1
	NO_2	50 PPM	0.0	9.2
	NO	1000 PPM	5.3	5.6
	SO_2	3000 PPM	1.7	6.8
	N_2O	250 PPM	250	250
		TOTAL	292.4	272.9
	without scrubbing	% ERROR	17.0%	9.2%
	with scrubbing	% ERROR	16.3%	2.8%

3.3 N_2O Measurement by Fine Line IR Absorption

The last presentation of this portion of the meeting was from Dr. Mark Zahniser of Aerodyne Research who discussed the use of fine-line lasers to measure N_2O. The absorption bands of N_2O at 4.5 and 7.8 microns consist of a large number of narrow lines, too closely spaced to be resolved by classical spectroscopic means. A tunable diode laser, however, can emit light that is monochromatic within 10^{-4} cm^{-1}. If the pressure of a sample gas containing N_2O is reduced to roughly 10 torr, the phenomenon known as pressure broadening is avoided; i.e., the individual lines in the N_2O absorption bands become sufficiently narrow so that they do not overlap. Thus by tuning the diode laser across an absorption band one can obtain a spectrum consisting of sharp nonoverlapping lines. While SO_2 and NO_2 and other gases also absorb light in this wavelength range, these absorptions will also consist of sharp lines, generally not overlapping the N_2O lines. Consequently the diode laser has the great advantage that it is inherently capable of measuring N_2O accurately without interference from other gases.

It also has the advantage of high sensitivity; e.g., in measurements in a discharge flow system, study of the reaction $NCO + NO = N_2O + CO$ the detection limit for N_2O was 10^9 molecules per cc. There are the further advantages of continuous rapid measurement of N_2O and being able to monitor the average amount of N_2O along a pathlength of several meters. These properties allow diode laser systems to measure N_2O emissions in systems which would be difficult if not impossible to characterize by other means; for example, the open field burning of agricultural wastes.

These advantages are, however, in part offset by two severe disadvantages: cost and difficulty of operation. Laser diodes are very much research tools, expensive, easily damaged by misuse, and shortlived even when given the best possible handling. The level of skill necessary to run such a system is high and even with such skill the apparatus requires a great deal of time and attention from its user. Accordingly, one aspect of Aerodyne's planned program in this area involves the development of a gas discharge N_2O laser which hopefully could be cheaper and more nearly troublefree. Some

recent advances may, however, improve the attractiveness of the tunable diode laser. The laser can be operated in a single mode at a power of up to 1 mW. The system can also be run at 77 K, which allows nitrogen cycle cooling to replace the much more troublesome helium cycle.

3.4 Measurement Summary

During the course of these presentations and the subsequent discussions a consensus seemed to develop on one important issue. The feeling was widespread, if not universal, that the technology for ambient monitoring of N_2O was in far better condition than that for source monitoring. Part of the reason for this situation was institutional. Ambient monitoring has been done in large ongoing programs, programs of sufficient size and duration so that the skills necessary for doing this difficult GC determination accurately could be fully mastered. The determination of N_2O emissions from combustion systems, however, has all too often been a matter of grabbing a few samples during the course of a program whose main objectives were not related to N_2O.

The second difficulty with the determination of N_2O from combustion sources relates to the nature of the sources themselves. While the ambient N_2O concentration at any given location does not vary observably during the time necessary to run a GC, one might reasonably fear that the concentration of N_2O being produced by a combustion source will fluctuate on a time scale that is short compared to the time for GC measurement. Mechanisms for producing N_2O during combustion discussed in the next section strongly suggest that such fluctuations may occur. Unfortunately, without a good continuous N_2O sampling and measurement system (similar to other source gas analysis systems) one is blind to such fluctuations and cannot really see how N_2O production behaves during combustion.

4.0 COMBUSTION SOURCES OF N_2O

4.1 Background

The discovery that combustion systems can generate N_2O and indeed are major sources of N_2O came as something of a surprise to the technical community. The products of combustion are in general what one would expect from considerations of high temperature thermodynamics. The equilibrium $N_2 + O_2 = 2NO$ is quite unfavorable under ambient conditions but becomes favorable under the high temperature oxidizing conditions reached in combustion systems. Thus it is no surprise that the major fixed nitrogen species formed in combustion is NO. The amount of NO formed in combustion is less than that which would be expected at thermodynamic equilibrium due to chemical kinetic constraints. For fuels which contain large amounts of fixed nitrogen, however, a superequilibrium amount of NO may appear. This, also, is due to chemical kinetics. Combustion flue gases from fuels that contain nitrogen may under some conditions contain traces of HCN and NH_3. This also is no surprise since combustion systems normally have regions of high temperature that are fuel rich and in such regions HCN and NH_3 are thermodynamically stable. The formation of N_2O, however, is not thermodynamically favorable under either oxidizing or reducing conditions at either high or low temperatures. Thus its presence is a thermodynamic puzzle.

This N_2O puzzle is compounded when one examines the situation from a kinetic viewpoint. In recent years there has been great progress in the use of computers for kinetic modeling of combustion systems; i.e., the description of the chemical behavior of combustion systems in terms of a set of elementary reaction equations that are solved by computer. Calculations of this kind have been done for the production and destruction of N_2O in flames with results which were presented in detail at the previous N_2O workshop and which are quoted herewith in Figures 5 and 6. Large numbers of calculations similar to those shown in Figure 5 were also done in order to learn which aspects of the results were due to specific details of the assumptions made regarding the reaction kinetics and which were the consequence of the general kinetic situation. This analysis led to a very

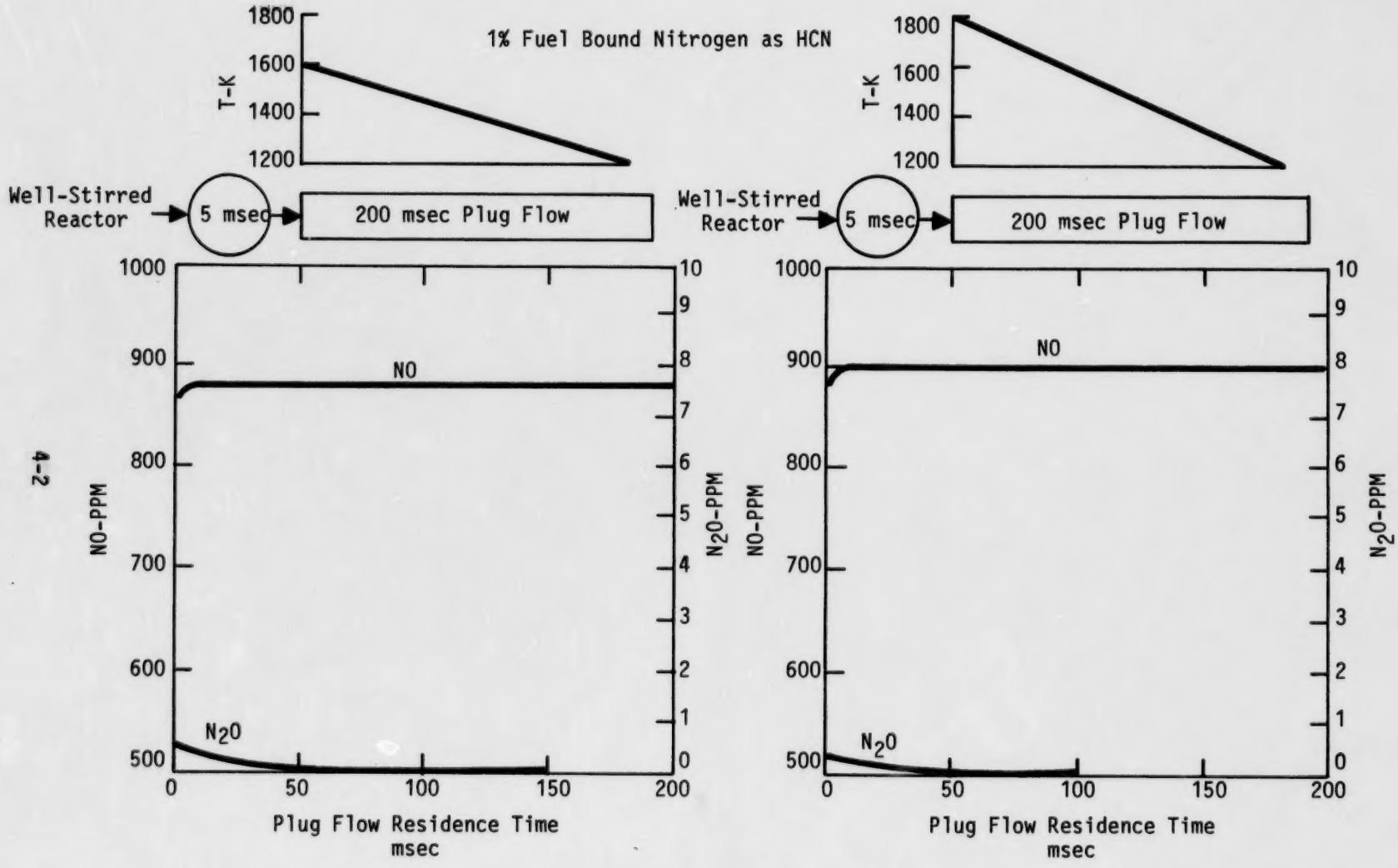


Figure 5. NO and N_2O profiles in a plug flow reactor for two temperature profiles with N_2O formation, ignoring formation by NCO + NO.

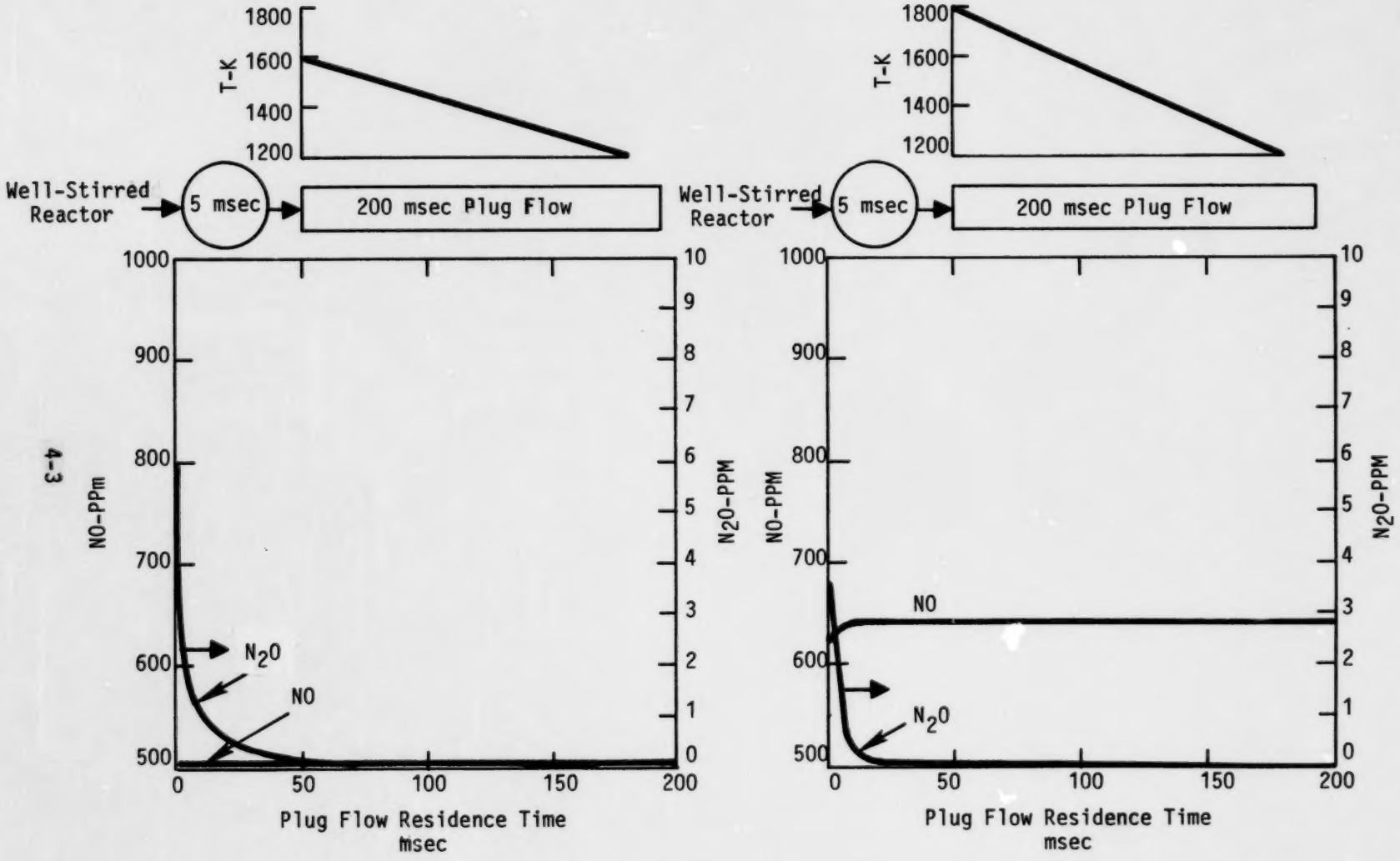


Figure 6. NO and N_2O profiles in a plug flow reactor for two temperature profiles with N_2O formation, including formation by NCO + NO.

puzzling conclusion. The production of N_2O in flames was not in itself a mystery. Figure 7 shows the generally accepted mechanism for the oxidation of fuel bound nitrogen. The results shown in Figure 5 correspond to this mechanism before the new reaction NCO + NO = N_2O + CO was added. Those in Figure 6 correspond to the full mechanism. With or without this new reaction the mechanism is capable of converting a significant portion of the fuel nitrogen into N_2O initially. The initial production of N_2O, however, does not matter since irrespective of how much N_2O is formed initially, the reaction $N_2O + H = N_2 + OH$ consumes it all in a short time.

Thus the first workshop of N_2O concluded with an unsolved mystery: it was possible to explain the fact that contrary to thermodynamics, combustion systems could produce N_2O. One could not, however, explain how that N_2O could survive the combustion environment which produced it and be present in the discharged flue gases.

4.2 Mechanistic Studies of N_2O in Coal Flames

Dr. John Kramlich presented recent work from EER which provides one plausible explanation for the emission of N_2O from coal combustion. To do this Dr. Kramlich and his coworkers at EER used a combination of computer modeling and experimentation. They began by developing a more complex model of the combustion process. It is well known that during pulverized coal combustion only part of the coal is consumed in the volatile flame (i.e. in the region of peak temperature) and that the rest is converted to a char that is oxidized downstream of the flame. A substantial portion of the fuel-bound nitrogen is retained in the char. Accordingly, the new combustion model assumes that during combustion the coal/air mixture spends 0.001 second in a well-mixed reactor at high temperature. The well-mixed reactor provides an ignition source for the flame. The mixture next enters a plug flow reactor with a declining temperature profile. This reactor completes the volatile flame-zone reactions and includes the char oxidation chemistry. The model assumes the coal is rapidly partitioned into combustible volatiles and char; the reaction of the volatiles is largely completed early in the plug-flow reactor. The heterogeneous processes governing nitrogen behavior include:

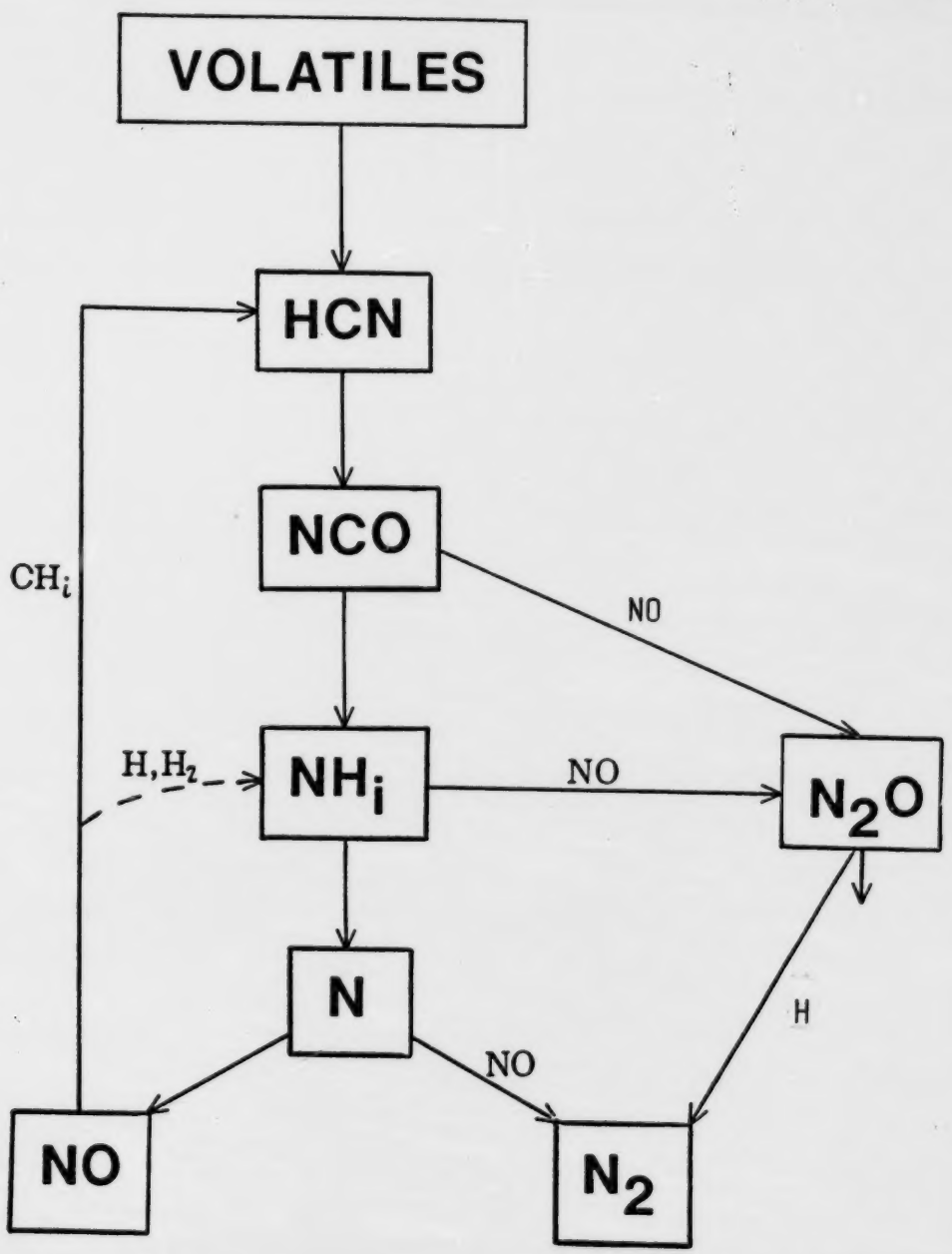


Figure 7. Mechanism for N_2O formation.

- Direct heterogeneous oxidation.
- Reaction with NO (i.e., reduction of NO on the char surface).
- Devolatilization of char nitrogen as HCN.

Each of these reactions proceed at rates selected from the literature. The net result was that only the devolatilization of HCN with its subsequent homogeneous conversion to N_2O could result in significant emissions. Heterogeneous NO reduction did not result in significant N_2O emissions, even if the unrealistic assumption is made that N_2O is the sole product of this reaction. Thus, the implication of the modeling was that the introduction of HCN in the post-flame gas phase could cause N_2O emission.

To study this behavior more closely, the model was simplified to remove the char chemistry, and provide for the artificial introduction of HCN at downstream locations. Figure 8 shows the configuration. Figure 9 shows the results of a set of calculations done with this model. If NH_3 is the introduced species, then under these conditions the yield of N_2O is trivially small. If, however, the nitrogen is introduced as HCN, the N_2O yield is critically dependent on the temperature (i.e. the point of introduction into the plug flow reactor) at which that introduction occurs. The HCN is oxidized by two routes:

$$HCN + OH = HNCO + H$$
$$HCN + O = NCO + H$$

Only the second yields N_2O through the precursor NCO. At low temperatures the first reaction is favored and although HCN is removed, little N_2O is formed. If the temperature is too high, the N_2O is largely destroyed by the $N_2O + H = N_2 + OH$ reaction. Within a narrow temperature range, however, HCN can be converted to N_2O with a high net efficiency. Figure 10 shows the results of a set of experiments done to check these modeling predictions; i.e. experiments in which natural gas doped with NH_3 was burned in a furnace to produce a flue gas which contained NO but no N_2O. Either HCN, NH_3, or CH_3CN (which decomposes to HCN) could be injected into the post-flame gases at positions corresponding to different temperatures. As predicted by the

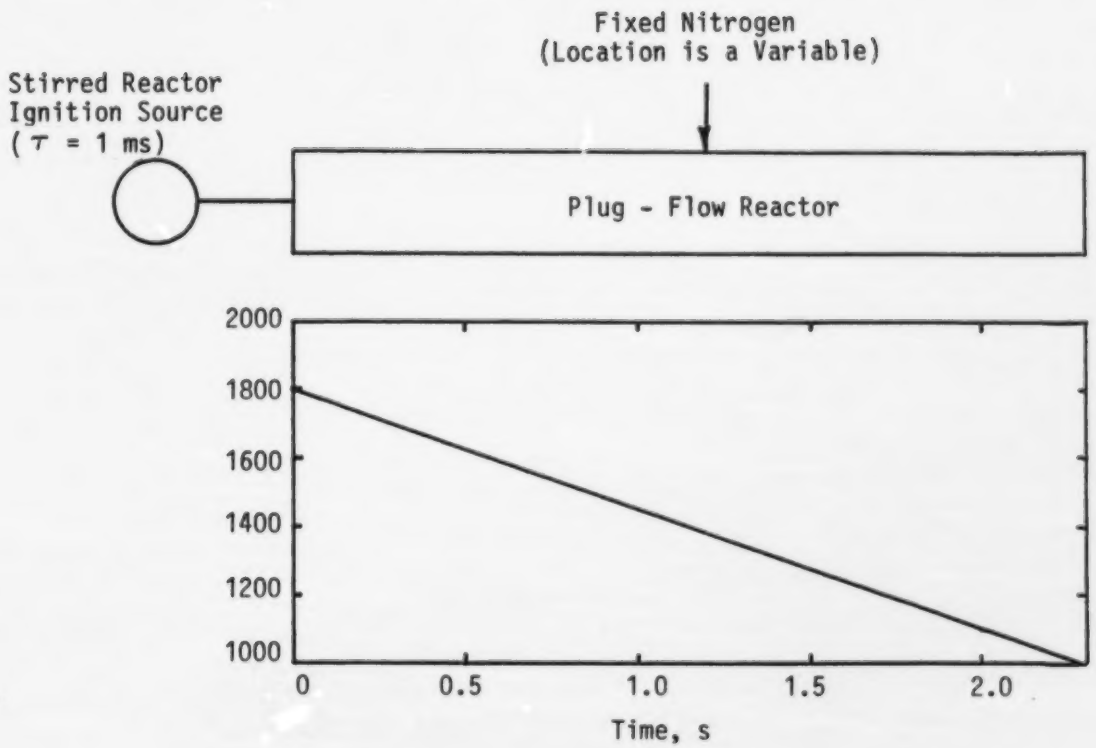


Figure 8. Setup for Computer modeling of N_2O formation during coal combustion with delayed release of fixed nitrogen by char.

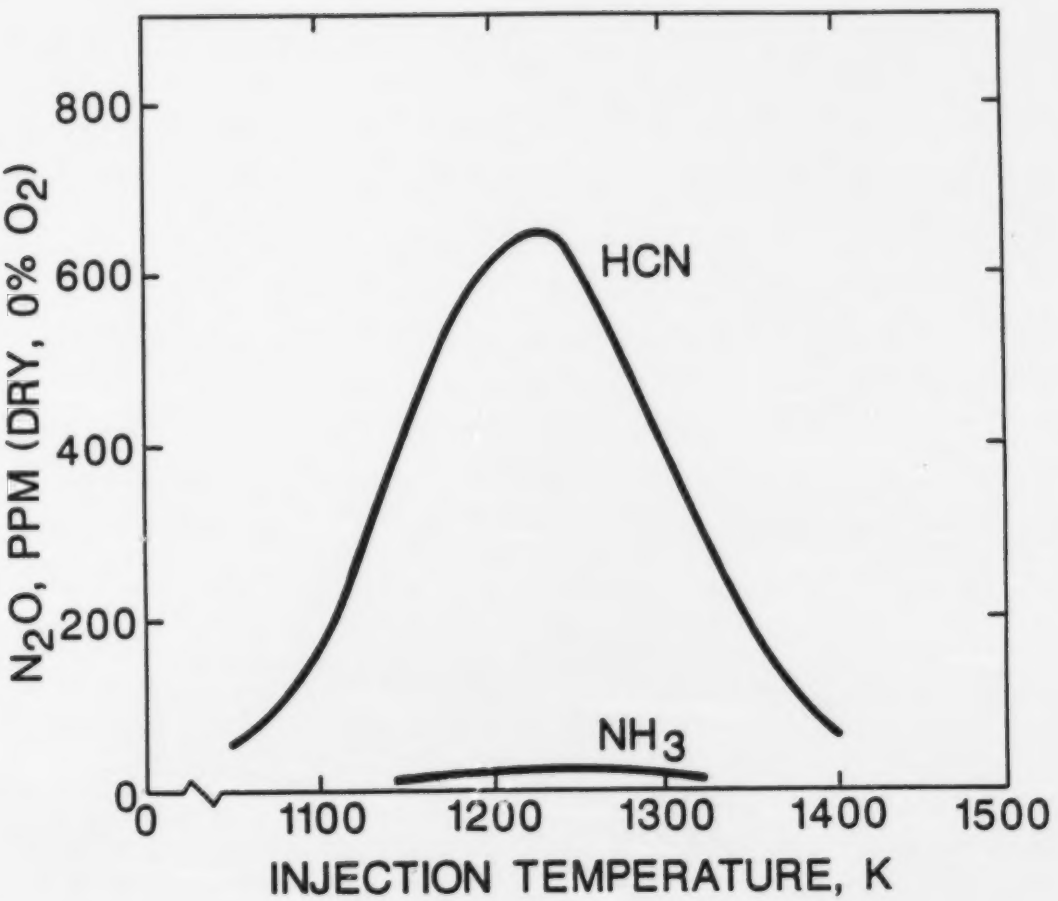
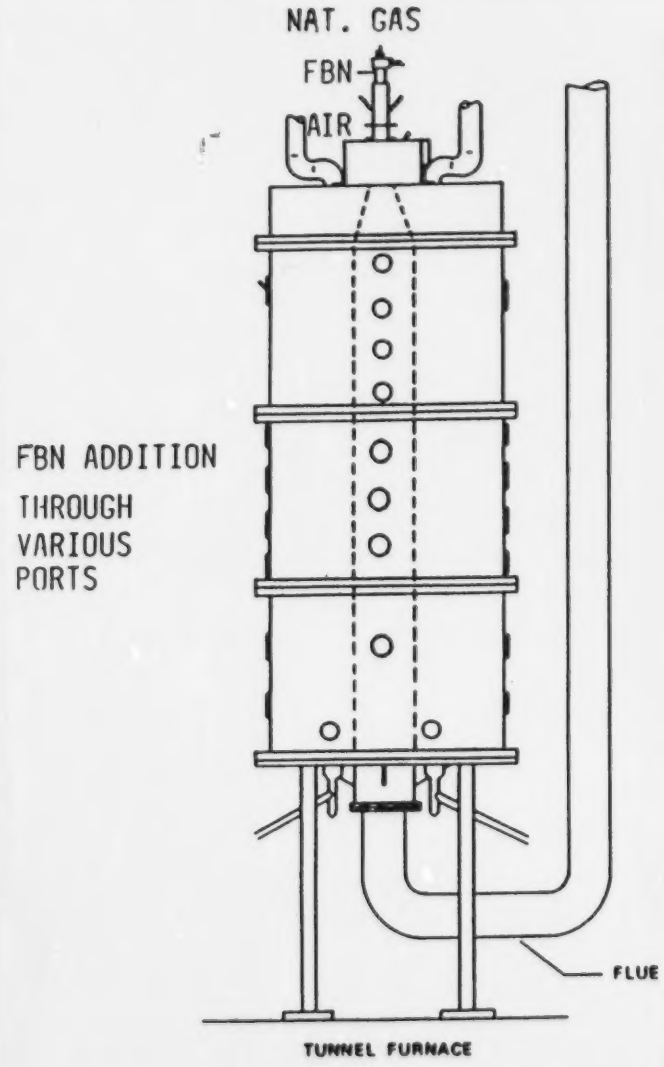


Figure 9. Calculated N_2O emissions as a function of HCN and NH_3 injection temperature.



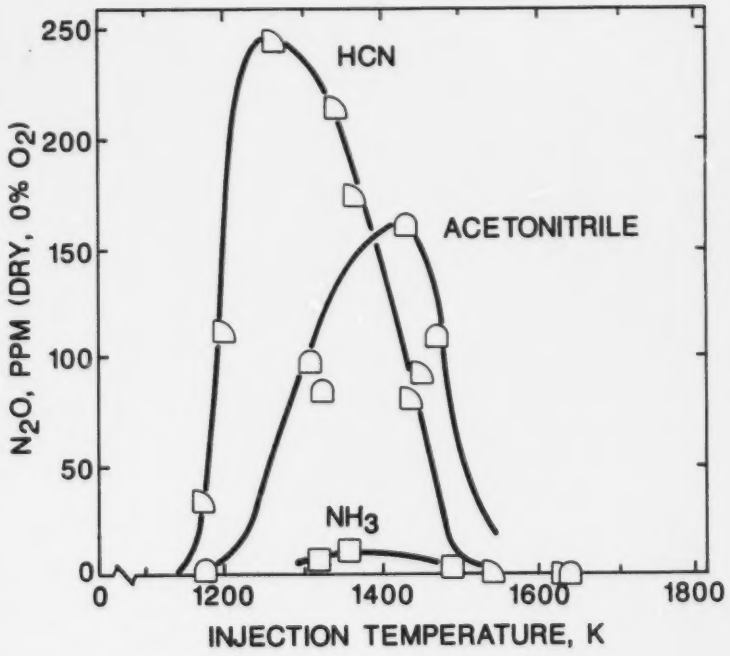


Figure 10. N_2O emissions as a function of fixed nitrogen addition at various reactor locations.

modeling calculations the injection of NH_3 yields little N_2O emissions, while at the optimum temperature HCN produces substantial amounts of N_2O.

During the discussion of this work Dr. Kramlich was the first to admit that while the work demonstrates a possible mechanism for N_2O production, it does not exclude all other possibilities. Thus, for example, in the EER mechanism for HCN production it is assumed that char nitrogen is converted to HCN by pyrolysis, a process dependent only on temperature. It seems possible, however, that the post-flame char undergoes gasification reactions which could also convert its nitrogen to HCN.

Dr. M. A. Toqan of MIT briefly reviewed the results of the Harvard/MIT work that was reported in detail at the last workshop. The reader is referred to that workshop report for a full discussion of these data. The results have also recently been published (Hao et al., 1987). Dr. Toqan also suggested that as an alternative to char providing the vehicle for carrying fixed nitrogen beyond the flame zone, imperfect mixing may also act this way. In industrial flames, large scale mixing is always an important rate-limiting process. If fuel-rich pockets containing cyano species are transported into cool fuel-lean regions, they may mix and react to form N_2O in a manner similar to that described by Dr. Kramlich.

Professor Jost Wendt of the University of Arizona made a brief presentation of a set of experiments in which a coal char is burned under accurately controlled conditions. If the EER mechanism is correct one would expect that there would be little or no net N_2O production in such experiments if the combustion temperature is above the window for HCN oxidation to N_2O, but copious N_2O production if it is within that window. The data available to date, Figure 11, confirm the former expectation.

One of the most important results discussed at the previous workshop was a study in which the N_2O production from a number of coal and oil-fired power plants was measured and correlated with the NO_x production; i.e., with some scatter it appeared that N_2O emissions were 25 percent of NO_x emissions. In his presentation Dr. Lanier reviewed both the data which was discussed at the

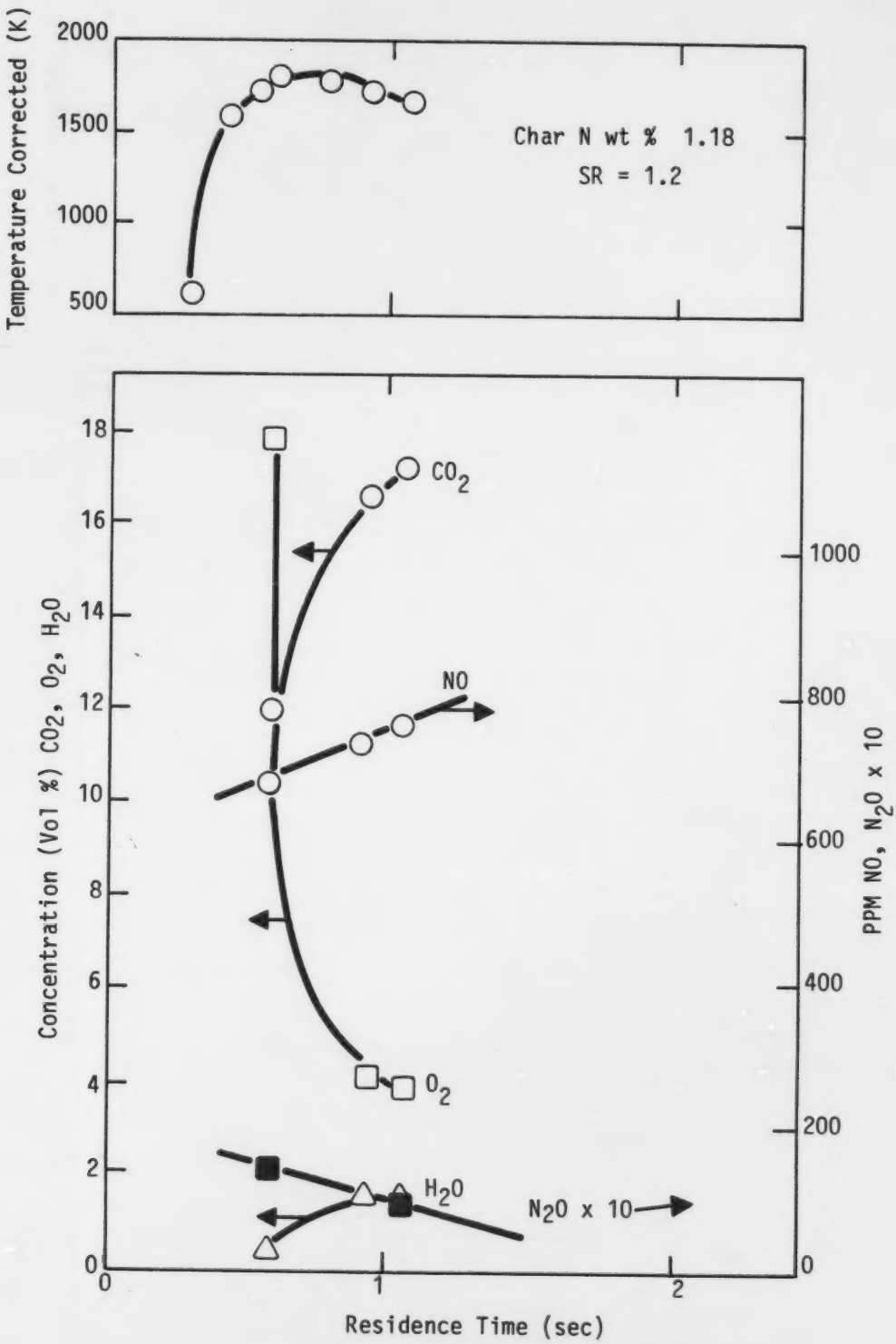


Figure 11. Temperature and major species profiles Utah bituminous char SR = 1.2; stoichiometric ratio = 1.2 and char-N = 1.18 wt. percent.

previous workshop and the results of subsequent measurements (Figure 12). (The EPRI results were supplied as a separate plot by Dr. L. Muzio of Fossil Energy Research.) Including the new data in the correlation greatly increases the scatter around the 25 percent line and lead Dr. Lanier to raise the question, was this correlation a reflection of some law of nature or was it an accident, i.e., an artifact of the particular boilers examined in the previous study? Dr. Lanier found most disturbing that one large German boiler had near-zero N_2O emissions despite having rather high NO_x emissions, strongly suggesting that the apparent correlation was completely accidental and without meaning.

The N_2O/NO_x correlation was the subject of considerable discussion, the group being divided into three schools of thought. Some took the viewpoint that while the correlation obviously had little if any fundamental meaning, it might still have some limited use. Specifically, they feel that despite the scatter the data in Figure 12 defined an approximate average value of N_2O/NO_x which could be used to estimate worldwide production of N_2O by combustion.

Another viewpoint was that the correlation was purely accidental, that its use purely as a statistical average was not justifiable since the data in Figure 12 did not represent a statistically valid sample of the world's combustion systems. Furthermore, in terms of controlling N_2O emissions the correlation was misleading, implying that any measure which decreased NO_x emissions would also decrease N_2O. In fact, the database is not yet sufficient to conclude that the reverse not true in some conditions.

The third school of thought was that the database is not yet sufficient to draw any conclusions.

Although coal can be burned in a variety of ways, all the data shown in Figure 12 represent only one method, pulverized coal firing. Thus, Dr. Muzio's report of pilot plant data for a different mode of coal combustion, cyclone burning, was of considerable interest to the workshop. In a cyclone furnace, as shown in Figure 13, crushed coal is burned in

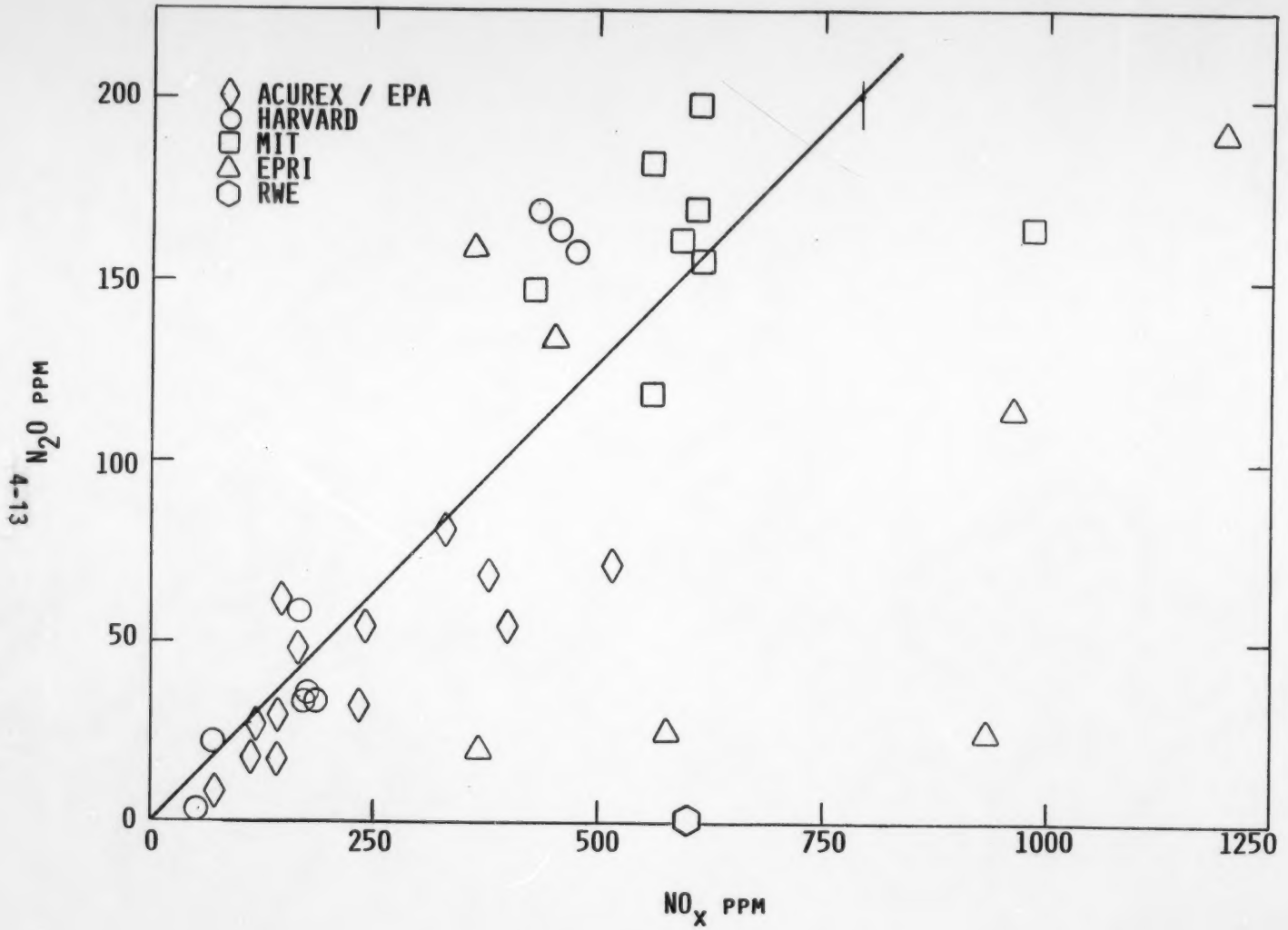


Figure 12. Field and pilot-scale data correlation of NO_x against N_2O.

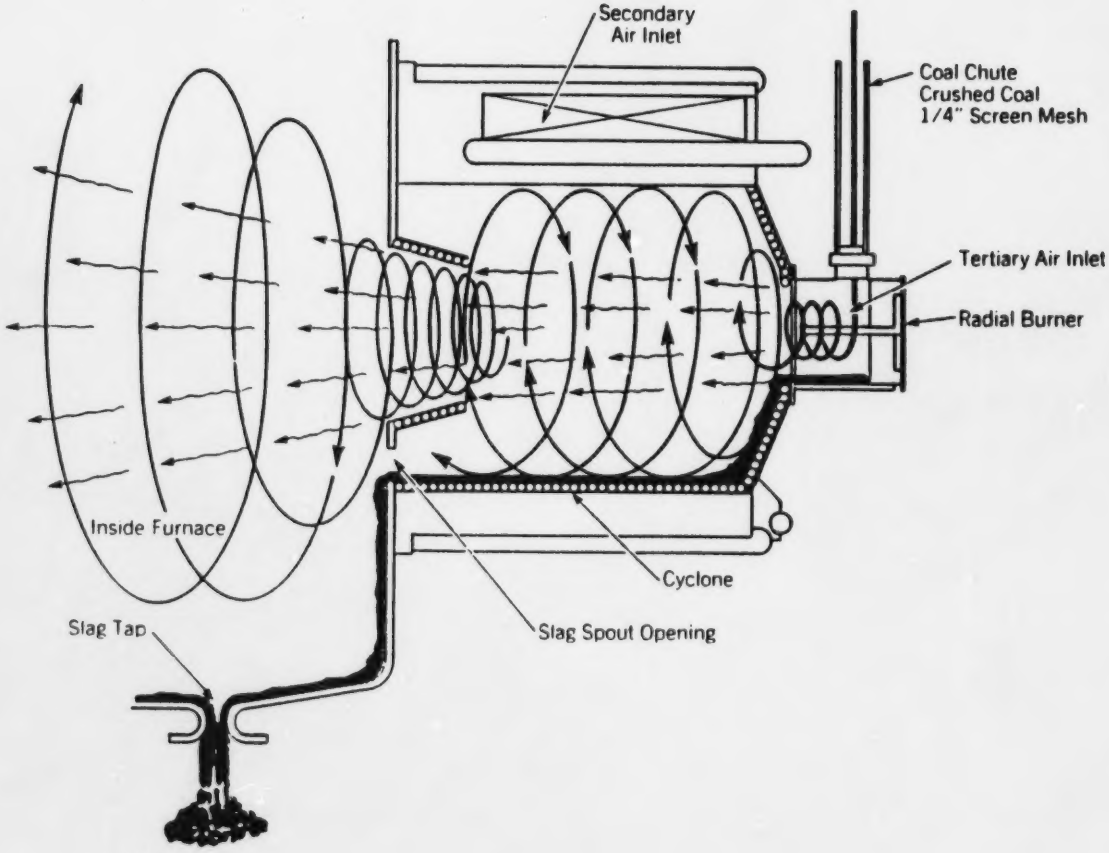


Figure 13. Cyclone furnace schematic.

intensely swirling gases. This very high-intensity combustion causes cyclone furnaces to produce higher than usual levels of NO_x but as shown in Table 8 the pilot cyclone combustor also exhibits a high N_2O/NO_x ratio. In fact, these N_2O values are among the highest ever reported for an industrial furnace or furnace simulator. The NO_x level of the cyclone furnace can be reduced by a process called reburning (injecting fuel into the post combustion gases to form a second flame) and as shown in Table 8 this method of NO_x control is also effective against N_2O, leading in this case to a proportional N_2O reduction. It should be emphasized that while the pilot-scale combustor simulates full-scale cyclone performance in terms of NO_x levels and slag rejection, it may not necessarily simulate the processes leading to N_2O formation in full-scale cyclone units. Nitrous oxide emission data from full-scale cyclone combustors are needed to verify the pilot-scale data.

Professor DeSoete offered his research plans for discussion. In his view an alternative to the EER mechanism is possible in which N_2O is produced directly by the oxidation of a nitrogen containing char. Much of the discussion centered on the potential difficulties of distinguishing between the direct oxidation of char nitrogen to N_2O and its conversion to HCN which then oxidizes to N_2O.

4.3 Homogeneous N_2O Chemistry in Flames

The results of the coal mechanistic work suggest that the actual formation of N_2O is due to gas-phase reactions. Heterogeneous or mixing processes only participate in delivering the precursors to an appropriate environment. Thus, homogeneous chemistry appears to be a key step in N_2O formation and destruction. A number of researchers are attempting to define the homogeneous reaction paths which govern N_2O concentrations in flames. The presentation given by Professor Bowman of Stanford University concerns his research group's studies by both experimental measurements and computer modeling of N_2O formation and destruction in fuel-rich laminar premixed flames. Figure 14 shows their experimental setup, Figure 15 shows the reaction pathways for N_2O formation and removal which were examined in their

TABLE 8. PRELIMINARY EPRI/B&W CYCLONE PILOT REBURNING
(PRIMARY FUEL: EASTERN BITUMINOUS COAL
REBURNING FUEL: NATURAL GAS)

Test Condition	Load 10^6 Btu/hr	NO_x ppm	N_2O ppm	N_2O/NO_x
Baseline--Full Load	6.0	920	484	0.53
Reburning* $(SR)_{cyclone} = 1.1$ $(SR)_{RB} = 0.9$	6.0	310	161	0.52
Baseline--Low Load	4.8	850	--	--
Reburning--Low Load $(SR)_{cyclone} = 1.1$ $(SR)_{RB} = 0.9$	4.8	260	36	0.14

*$(SR)_{cyclone}$: Stoichiometric ratio in the cyclone
$(SR)_{RB}$: Stoichiometric ratio after addition of the reburning fuel

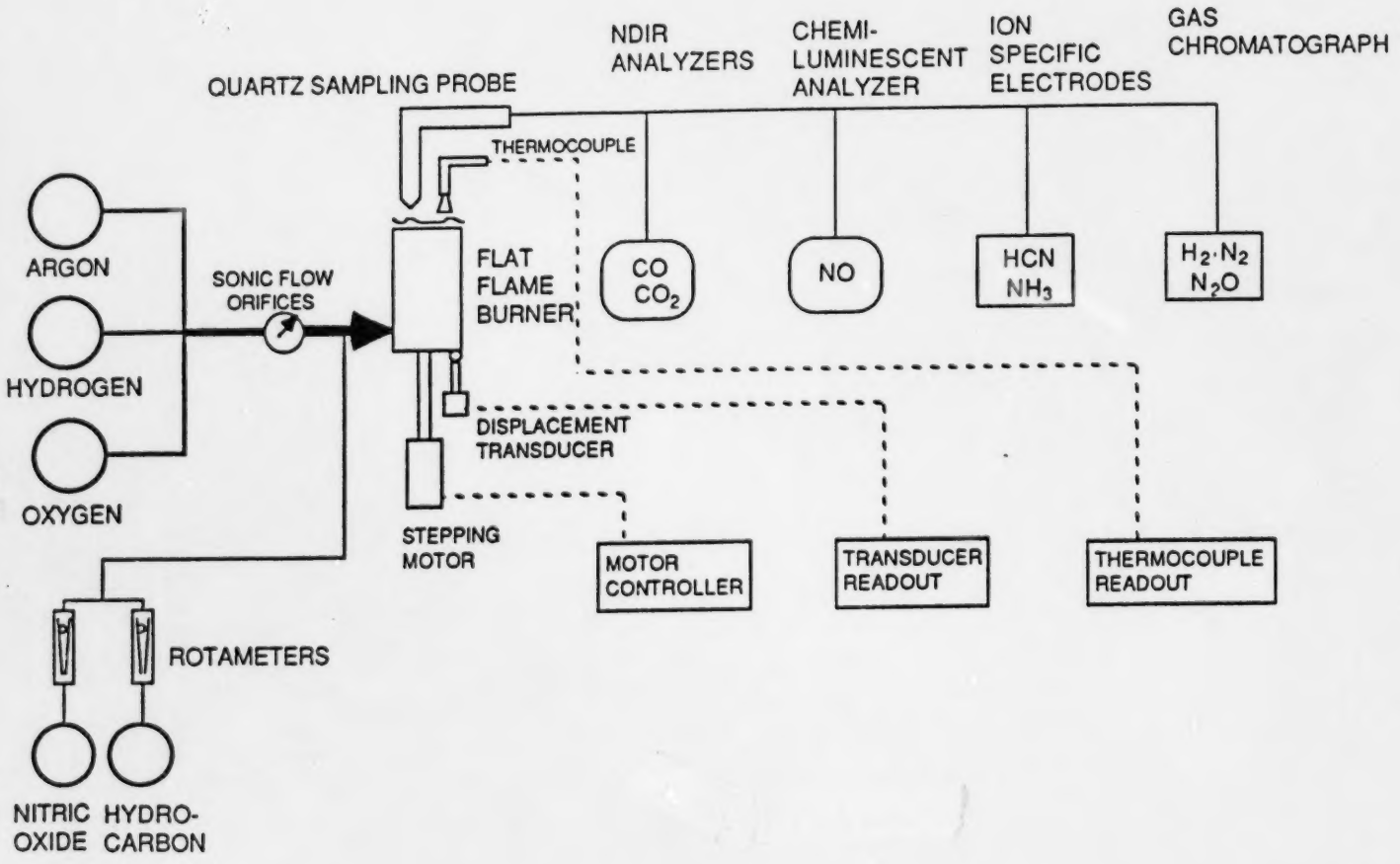


Figure 14. Apparatus used for the Stanford N_2O experiments.

$$NH + NO \rightarrow \begin{matrix} N_2O + H \\ N_2 + OH \end{matrix}$$

$$NH_2 + NO \rightarrow \begin{matrix} N_2H + OH \\ N_2 + H_2O \\ N_2O + H_2 \end{matrix}$$

$$NCO + NO \rightarrow \begin{matrix} N_2O + CO \\ N_2 + CO_2 \end{matrix}$$

$$N_2 + O + M \rightarrow N_2O + M$$

$$N_2O + H \rightarrow \begin{matrix} NO + NH \\ N_2 + OH \end{matrix}$$

Figure 15. Key reaction pathways for N_2O formation and destruction from the Stanford modeling.

modeling and Figures 16 and 17 show typical modeling results. Specifically Figure 16 shows that in a flame of CH_4/air doped with NO the major mode of N_2O formation is the NH + NO = N_2O + H reaction. In contrast for a flame doped with HCN (Figure 17) the major N_2O formation route is NCO + NO = N_2O + CO. For all flames Prof. Bowman finds that the dominant mode of N_2O removal is the N_2O + H = N_2 + OH reaction. Further, he finds that this reaction is so efficient at removing N_2O that for all conditions the net production of N_2O by laminar flat flames, i.e., the amount of N_2O in their exhaust, is very small.

Professor Bowman spent some time reviewing the state of knowledge of these principal elementary reactions. Figure 18 shows a compilation of the rate data for NH + NO. In general, most of the disagreement exists at the high temperatures. There is also some question on the product distribution. The energy diagram contained in Figure 18 shows that while N_2 + OH is the product distribution most favored in terms of exothermicity, its route involves a substantial energy barrier. Thus, a favored route may be presumed to yield N_2O + H. Figure 19 shows that the limited measurements published to date on NCO + NO are self-consistent. However, the data are not sufficient to determine if there is a temperature dependence at high temperature. Finally, Figure 20 shows that under flame conditions the rate of the principal N_2O destruction reaction, N_2O + H, is quite well-defined by existing data.

Professor Bowman concluded that since N_2O destruction in gas flame zones is so efficient, then the much larger net N_2O productions obtained in oil- and coal-fired utility boilers cannot be explained in terms of the chemistry of premixed laminar flames. Thus, Prof. Bowman supports the view that some mechanism beyond premixed homogeneous chemistry is clearly necessary. Professor Bowman also felt that the overall level of understanding of homogeneous N_2O chemistry in flames was much better than the general understanding of N_2O behavior in coal flames.

Dr. Nancy Brown discussed the work of her research group in two areas of importance to the workshop. One of these areas was the use of thermodynamic

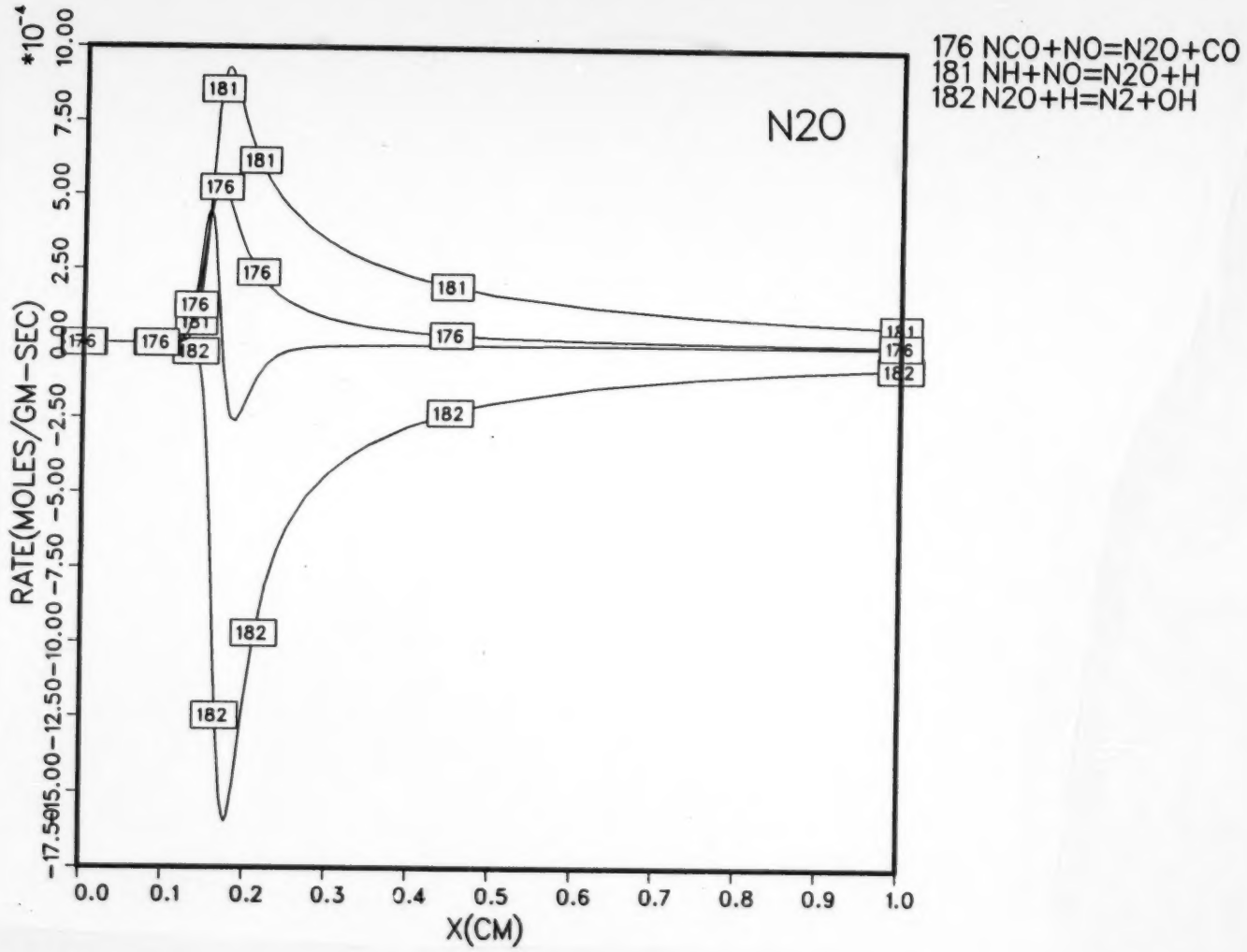


Figure 16. N_2O formation and destruction rates from modeling of an NO-doped methane flame (Roby, 1987).

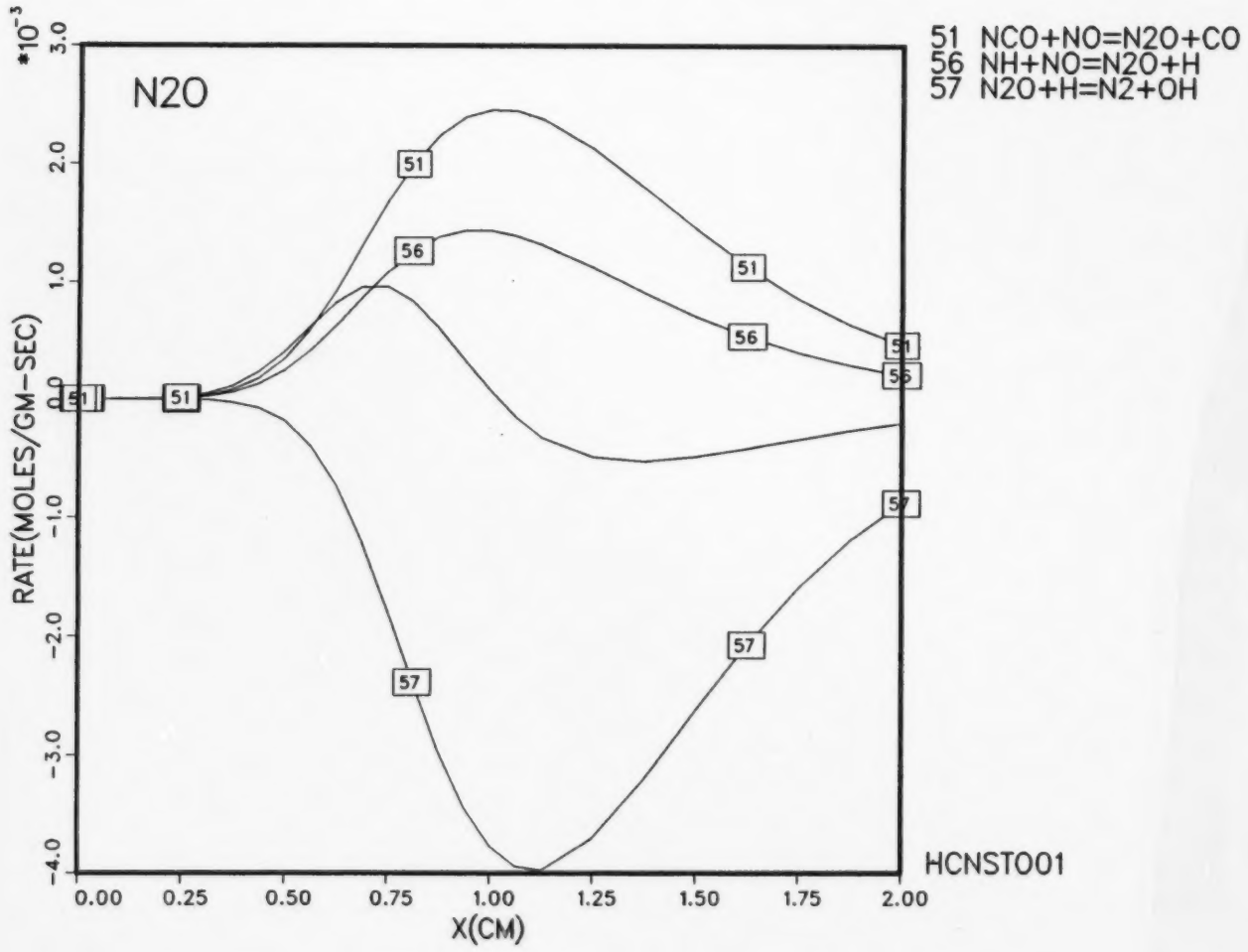


Figure 17. N_2O formation and destruction rates from modeling of an HCN-doped H_2 flame (Roby, 1987).

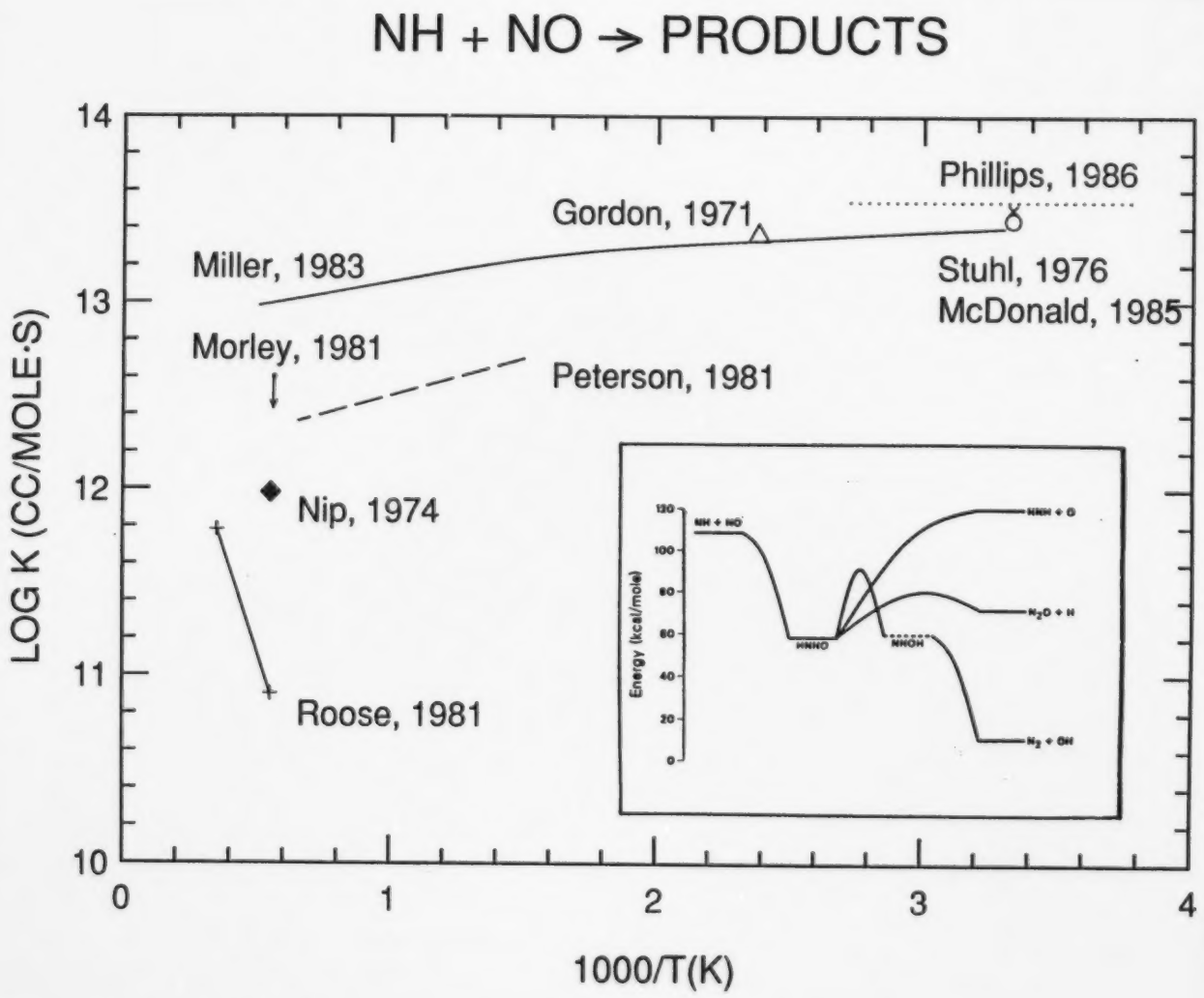


Figure 18. Rate constant compilation for NH + NO, and energy diagram for various intermediates and products (Roby, 1987).

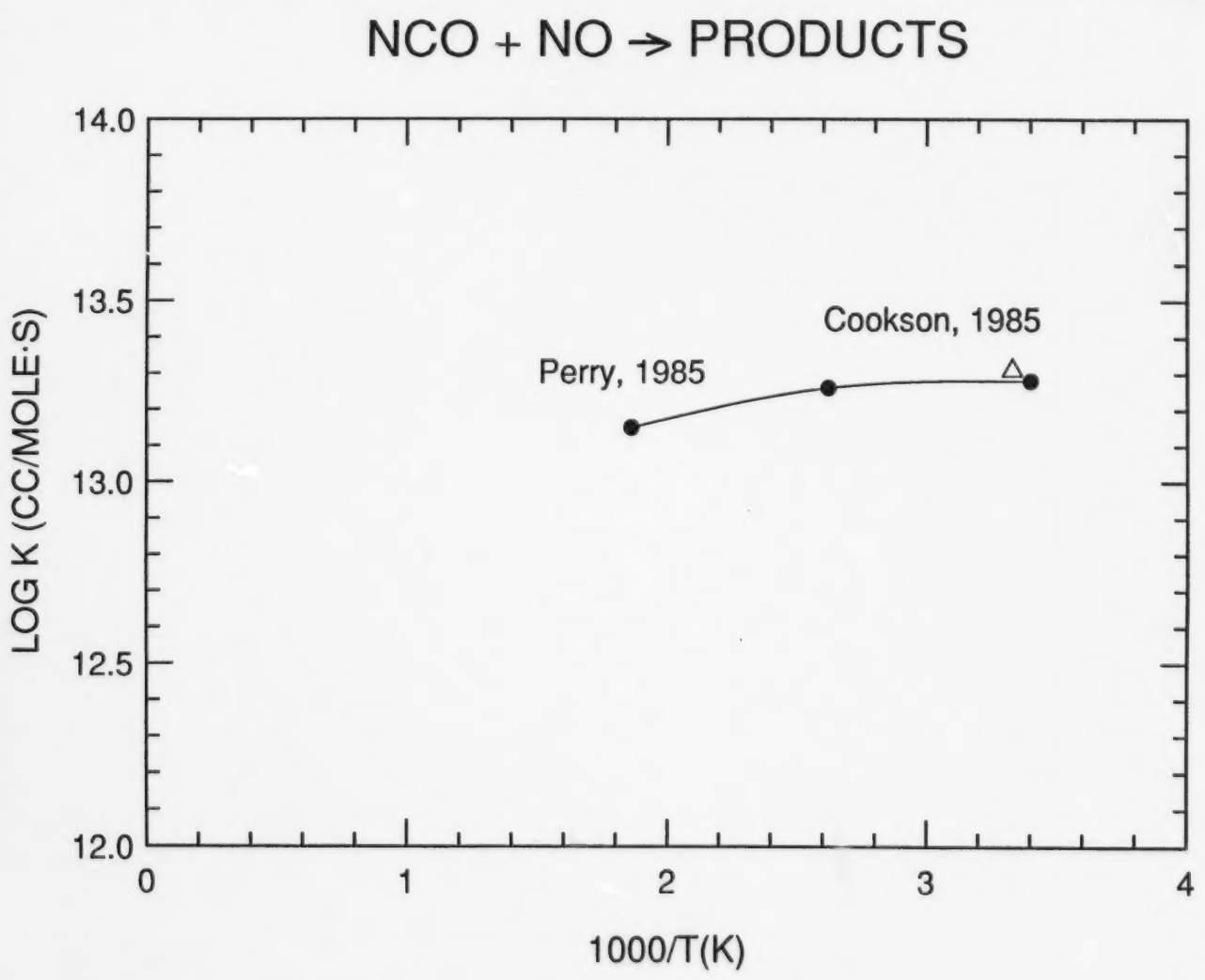


Figure 19. Rate constant compilation for NCO + NO (Roby, 1987).

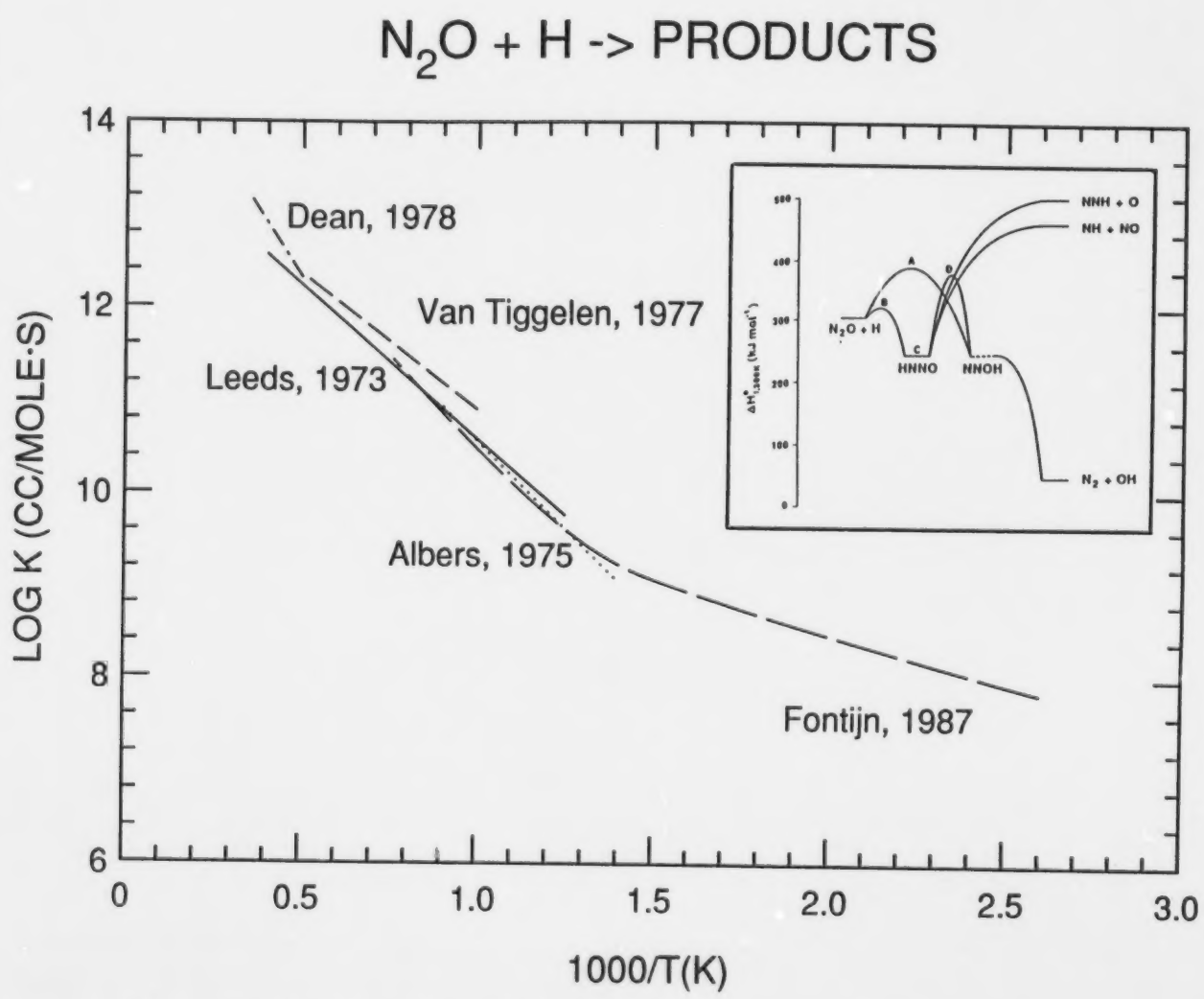


Figure 20. Rate constant compilation for N_2O + H, and energy diagram for various intermediates and products (Roby, 1987).

data in kinetic modeling. The computer codes used in modeling always assign a forward and a reverse rate to every reaction, the forward rate being an input parameter and the reverse rate being calculated from thermodynamic data. While it is all well and good for species whose thermodynamics are well known and generally agreed to, Professor Brown showed a number of cases in which the uncertainties for the thermodynamics of the species involved leads to significant uncertainties in the kinetics. In particular, there are uncertainties in the data for a number of key nitrogen species. Dr. Brown's message was to use as much care and attention in selecting thermodynamic data as one would use in selecting rate constants.

Dr. Brown also showed the results of her group's studies with premixed flat flames. In general her results are similar to Bowman's; i.e., she finds that while significant amounts of N_2O may be formed in the flame it does not survive long in the post-flame gas. This is shown in Figure 21, which is a radial profile taken 1.65 mm above a flat flame burner. Throughout the post-flame gases the N_2O levels are very low. As one approaches the edge, however, (i.e. enters the region in which the post-flame gases are being rapidly mixed with cold air) the N_2O level rises to a notable maximum. Some members of the workshop thought these results could be the basis of another explanation of N_2O formation in oil- and coal-fired boilers; i.e., they argued that N_2O and HCN could be formed in the flame and because of unusual mixing conditions they could be transported from this region. It is very probable due to poor spatial resolution in atmospheric pressure flames that peak N_2O concentrations in Brown's experiment were much larger than measured values. Dr. Brown stated that flame zones were very thin in this experiment and concentration gradients were very large. The probe measurements most likely reflect an average concentration over about five probe diameters. Others, however, argued that such a mechanism seemed quantitatively inadequate, that the peak concentration of N_2O in Brown's experiments was nearly an order of magnitude less than what can be found in boiler flue gases and that only a slight fraction of the gases in Brown's experiment contain even this limited amount of N_2O. Such a mechanism may well contribute to the 3-10 ppm of N_2O that is observed from industrial gas flames, however.

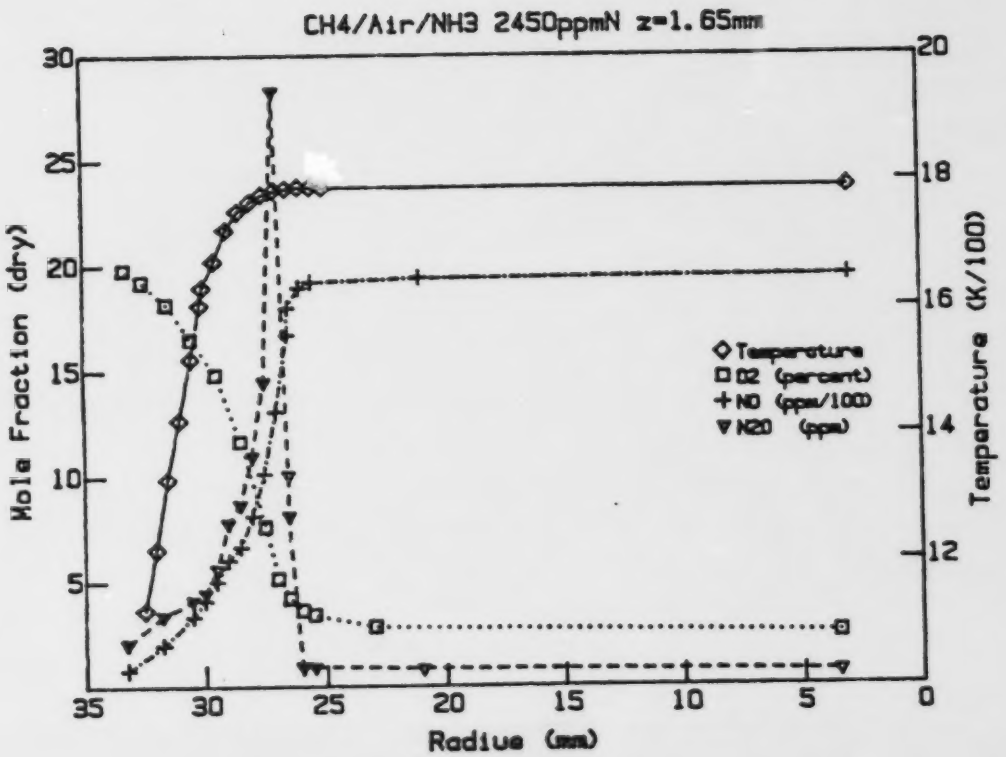


Figure 21. Radial temperature and concentration profiles at a height of 1.65 mm above the 6 cm. diameter burner.

One of the major concerns at both this and the previous workshop concerned the extent to which measures for control of NO_x also remove N_2O or increase it. At the previous workshop data were presented which showed that staged combustion was effective both for NO_x and N_2O control. Dr. Lyon's presentation concerned the effect of the Thermal $DeNO_x$ process on N_2O levels. Laboratory experiments done early in the development of the Thermal $DeNO_x$ process showed that it did not produce significant amounts of N_2O. Recently reported field tests, however, show that when the process was installed on a boiler with significant N_2O emissions, the process achieved a reduction of N_2O which was greater than the NO_x reduction. Dr. Lyon and coworkers have developed a kinetic model of Thermal $DeNO_x$ process which describes its behavior quite accurately but it was not possible to explain a removal of N_2O in terms of this model. It is possible that the Thermal $DeNO_x$ Process acted to either (1) remove the HCN precursor, or (2) prevent its reaction into N_2O.

Professor Houser of Western Michigan University discussed the results he has obtained studying the oxidation of HCN in laboratory flow reactors, both plug flow and well-stirred. In agreement with the EER results presented by Kramlich, Houser finds that the oxidation of HCN at sub-flame temperatures can produce substantial yields of N_2O. The conditions of Houser's experiments, however, are too different from those used in the EER work to permit detailed comparison. Professor Houser also presented two additional interesting results. First, an inverse relationship was observed in the yields of N_2O and NO, i.e., flame conditions were necessary to form NO while sub-flame conditions promoted N_2O formation. Second, the rate constants for the NCO/O and NCO/NO reactions, which have been proposed to be those most likely to form NO and N_2O, respectively, would require impossibly high oxygen atom concentrations to reduce the N_2O yields to negligible amounts under Prof. Houser's conditions. However, large NO yields accompanied by negligible amounts of N_2O were found over a wide range of conditions. These observations, in addition to results from the oxidation of N_2O and of HCN/H_2 mixtures support the conclusion that N_2O and NO were formed from a common precursor, and that there must be a non-sequential pathway contributing to the formation of both. Such a conclusion would reduce the importance of the NCO/NO reaction as the primary source of N_2O.

5.0 CONCLUSIONS AND IMPLICATIONS

The general summary, conclusions, and recommendations from each of the major topic areas are collected below.

Summary of Conclusions. Since the previous workshop there has been significant progress on a number of aspects of the N_2O problem and a number of important conclusions now seem relatively well established if not absolutely proven.

Importance of the N_2O Problem. All of the major modeling studies done to date show that both global warming due to increasing greenhouse effect and ozone depletion are potentially severe long-term problems and that N_2O is important in both problems.

5.1 Measurement of N_2O

The technology of ambient monitoring of N_2O appears to be in a satisfactory condition. This technology can also be applied to source monitoring; however, certain difficulties render this approach less satisfactory. The difficult GC determination is best performed by groups with long-term commitments to measurement. While this is the case for the researchers in ambient air analysis, frequently source testing involves short-term/high-intensity efforts. Any lack of long-term commitment can invite error. Secondly, for observing N_2O from combustion sources one would greatly prefer a technique with better time resolution than GC since there are reasons to expect that combustion N_2O undergoes substantial short-time fluctuations.

Anthropogenic Sources of N_2O. Perhaps the most important and certainly the most startling new facts presented at the meeting was the presentation by Dr. Rasmussen showing that the current increase in N_2O levels began not at the start of the industrial revolution but somewhat after World War II. While this result might be interpreted in terms of changing agricultural practices, the more likely explanation would appear to be changing combustion

technology. The period in question corresponds to a time when the world's electricity generating capacity was increasing rapidly, the major proportion of this increase being pulverized coal firing of coal. Of course, a number of other industrial processes, such as fluid bed catalytic cracking, also enjoyed greatly expanding usage during this time period, as have other anthropogenic activities such as gasoline use, clearing of tropical forests, and increased nitrogen fertilizer use.

Two of the presentations given at the workshop involved spectroscopic determination of N_2O and it is to be hoped that work of this general nature will continue since there are a variety of needs such as response time which cannot be met by GC techniques.

5.2 Combustion Sources of N_2O

While some of the details of how N_2O is formed during the combustion process remain unclear, the broad outline of the process seems to be generally agreed to. While combustion systems can produce substantial amounts of NO by thermal fixation of nitrogen (thermal NO_x), direct thermal production of N_2O seems to be a very minor process. Like fuel NO_x, N_2O production is related to the amount of chemically bound nitrogen present in the fuel. It appears, however, to be much more sensitive to how the fuel is burned. At peak combustion temperatures, i.e. within the flame itself, N_2O is a very short-lived species. Consequently, while some N_2O emission may involve the rapid removal and quenching of N_2O formed within the flame zone, it seems that most N_2O emissions are the result of N_2O precursors which escape the flame zone and react subsequently at downstream positions where the temperature is lower. These precursors may be either HCN or nitrogenous char. If the char is chiefly responsible for N_2O, it may be forming the N_2O by direct heterogeneous oxidation or by forming HCN which subsequently oxidizes to N_2O. Further, this conversion of char nitrogen to HCN may involve either pyrolysis or gasification, two quite distinct reaction pathways.

While there are thus a variety of possibilities, still even with these details missing this general mechanism has a number of important implications.

Firstly, it is clear that since N_2O emissions are a sensitive function of how the fuel is burned and not directly related to NO_x production, there is no substitute for direct N_2O measurements. Unfortunately, the presently available data are painfully incomplete. In estimating which combustion systems might have greater or lesser N_2O emissions one should be guided not by the NO_x which the system produces but rather by the amount of fuel nitrogen being fed to the system.

Secondly, it seems very possible that combustion systems in which the fuel is burned at temperatures substantially less than flame temperatures, e.g. fluidized bed combustors, may well have high N_2O emissions relative to systems that burn via flames.

Thirdly, it is to be noted that in attempting to design burners which will operate with lower NO_x production, one commonly used approach is to make the combustion less intense, to stretch out the flame. Such an approach can decrease the extent to which combustion is completed within the flame and hence increased the extent of post flame reaction. Again major increases in N_2O production seem possible.

As possible conclusions to the discussions, Dr. Lanier proposed three general statements of needs. Following discussion and minor word changes, these statements met with general approval. They were:

1. Given the critical nature of the potential problem there is a need to establish a scientifically defensible data base related to combustion generated N_2O.

2. The current data base on emission factors is inadequate to establish the contribution of combustion-generated N_2O to the total global budget.

3. There is a need to establish a broad-based coordinated combustion-generated N_2O program with:

- Full-scale--Data base
  - Emission factors
  - Mechanistic insight

- Pilot-scale--Guide and interpret
  - Laboratory-scale--Guide and interpret
  - Instrumentation--Standardize

It was the strongly held position of the majority of the scientists at the workshop that our current knowledge of N_2O production during combustion is inadequate to make defensible N_2O emission predictions on either a global or site specific basis. Certain trends appear to be emerging, such as lower N_2O emissions from lignite and brown-coal-fired boilers, but the data base is far too limited to accept these trends a proven facts (field samples from one or two boilers firing low rank coal and operating with undefined conditons). If these trends can be substantiated with additional field measurements a more accurate assessment of the contribution of combustion generated N_2O to the global flux should be possible.

Published estimates of the global flux of N_2O from combustion have been made by combining projections on world fuel use with estimates of N_2O produced during combustion of that fuel. The ratio of N_2O emitted per unit of fuel burned is generally accomplished as a two step process in which the estimated ratio of N_2O/NO_x is multiplied by an estimate of NO_x emitted per unit fuel input to the boiler (e.g. an NO_x emission factor from a publication such as AP-42). Estimation of N_2O production per unit fuel burned based on an upper bound from the current data (see Figure 12) results in a projection that large boiler N_2O emissions account for essentially all of the anthropogenic N_2O flux to the atmosphere (assessment by R.A. Rammussen of the data contained in Hao et al., 1987). However, the lower bounds on the available data tend to indicate that large boiler N_2O emissions are a negligible contributor to the total anthropogenic flux. A further

anthropogenic flux. A further complication to this issue is the total lack of data on N_2O emissions from fluid bed catalytic cracking. During the meeting it was pointed out that a substantial fraction of the world's oil production goes to catalytic crackers and that in the process most of the nitrogen present in the oil is converted to nitrogen containing coke. To regenerate the catalyst and to provide process heat this coke is burned in a fluidized bed at temperatures low enough so that any N_2O formed should be expected to survive. Thus, whatever the mechanism, if the conversion of char nitrogen to N_2O is efficient, then fluid bed cat cracking may cause emissions which are out of proportion to the amount of fuel burned in the process.

Of course, the above is only an example. The concern of the workshop is that existing combustion systems and the fuels used in them are a widely varying group which has not been examined in sufficient detail. Similarly there was a strong feeling within the workshop that it is important to know what, if any, N_2O problems of emerging new combustion technologies have early in their development. These technologies include fluid bed combustion and many methods of controlling the NO_x emissions from combustion systems such as selective catalytic reduction.

These conclusions lead to two immediate recommendations for action:

Characterization of the N_2O Emissions of Different Combustion Systems

The measurement of N_2O from combustion sources can be done with the same high precision as has been achieved in ambient monitoring, provided one is willing to mount a coherent measurement program, a program of sufficient scope, stability, and continuity so that the necessary GC expertise can be developed. A program of that kind is also what is clearly needed to define the N_2O emissions of the many different kinds of combustion systems and fuels which may be contributing to the N_2O problem. In addition to the problem of defining the N_2O emissions of existing combustion systems it is also important to define the N_2O emissions of new combustion technologies before they are widely implemented.

Mechanism of N_2O Combustion Chemistry

While some aspects of the mechanism are now clear, a relatively modest further effort could spell out the N_2O mechanism in quantitative detail. Such a quantitative mechanism would put the N_2O problem of the same basis as soot and CO, i.e. the factors which govern the burnout of soot and CO are well understood and combustion engineers know what must be done to keep these emissions down to tolerable levels. A similar understanding of N_2O formation would allow the development of combustion systems which are satisfactory in all respects, including minimizing N_2O production.

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APPENDIX A

Overview

of

The Atmospheric Stabilization Framework

prepared by

William Pepper

ICF Incorporated

and

Daniel A. Lashof

Office of Policy, Planning, and Evaluation

U.S. Environmental Protection Agency

February 19, 1988

Introduction

The U.S. Environmental Protection Agency has been asked by Congress to report on the environmental effects of global climate change and the choices the global community may need to consider in order to both limit and adapt to potential global warming. This document is a brief outline of the framework that EPA is developing to assess the prospects for stabilizing the concentrations of climate-modifying trace gases in response to the Congressional request. It is expected that this framework will undergo continuing refinement and use as EPA assesses the relative effectiveness of different strategies that may be considered under the Climate Protection Act.

The Atmospheric Stabilization Framework is a tool for integrating data and models for the purpose of assessing strategies for limiting the "greenhouse" warming that is predicted to occur over the next several decades due to the accumulation of trace gases in the atmosphere. The gases that contribute directly or indirectly to warming include CO_2, CO, CH_4, N_2O, NO_x, and CFCs. The Framework allows analysts to estimate emissions of greenhouse gases from both anthropogenic and natural sources, and the effect of these gases on global warming through the year 2100 based on assumptions about patterns of economic development and control strategies.

Integrating Framework

The integrating framework consists of six modules as follows:

- Energy Module
  - global energy forecasting model
  - global end-use database/model
  - energy emission coefficients
- Industry Module
  - CFC emissions model
  - other industrial sources
- Agriculture Module
  - global agricultural activity model
  - agricultural emissions coefficients
- Land-Use and Natural Source Module

- Ocean Module
- Atmospheric Composition Module

Figure 1 illustrates the integrating framework. The four emissions modules use input data including scenario specifications for population growth, productivity, etc. to estimate emissions of greenhouse gases for nine regions of the globe. Emissions are calculated every five year from 1985 to 2025 and then every 25 years through 2100. The atmospheric composition and ocean modules together estimate global concentrations of the greenhouse gases resulting from the projected emissions, and increases in global temperatures resulting from the calculated concentrations. The atmospheric trace gas concentrations and temperatures feed back to the emissions and concentration modules for the next time period.

Energy Module

The energy module consists of a Global Energy Forecasting Model (GEFM) developed at ICF based on the energy-CO_2 model of Edmonds & Reiley (1983, 1986), a Global Energy End-Use Model (GEEM) developed by WRI and LBL for this study, and combustion emission coefficients developed for this study. The two energy models provide alternative approaches to forecasting consumption patterns and have different input and output needs. Initially, input specifications will be developed so that these two models produce consistent results. The GEFM balances supply and demand based on estimates of total resources and macro-economic estimate of demand. The GEEM estimates demand based on consumption of specific energy services and technical efficiency. Since the end-use model does not project supply, the GEFM will be used to project fuel mix and supply prices in all cases. The end-use model provides an alternative approach to projecting energy demand based on explicit assumptions regarding technical and structural change. In any case the final fuel consumption is allocated among the individual combustion technologies for which emission coefficients are available in order to calculate trace gas emissions. Additional emissions associated with fuel production are also estimated.

Industry Module

The industry module consists of a CFC model and a model for other non-combustion trace gas sources. The CFC model was developed by EPA for use in assessing stratospheric ozone

depletion. It projects production and emissions of the following compounds:

- o CFC-11
- o CFC-12
- o CFC-22
- o CFC-113
- o CCl_4
- o CH_3CCl_3
- o Halon 1211
- o Halon 1301

Other industrial sources of trace gases include landfills, cement production, and other non-biogenic activities. The model that estimates these sources uses the following type of equation to represent emissions for each region (where regional breakouts are possible):

$$EMISSION_g = CONSTANT_g * POP^a * GDP^b$$

Where "g" represents the trace gas, "POP" represents the regional population, "a" represents the elasticity of the emissions to growth in population, "GDP" represents the per-capita GDP, and "b" represents the elasticity of emissions to growth in per-capita GDP.

Agriculture Module

The agricultural Module uses the IIASA/IOWA Basic Linked System (BLS, Frohberg, 1988) to forecast land-use, fertilizer use, and agricultural production for 34 different regions. These estimates are aggregated to nine global regions and used with emission coefficients to calculate emissions of greenhouse. Emissions will be estimated for:

- o N_2O from fertilizer use
- o CH_4 from rice production and enteric fermentation in domestic animals

Emissions from biomass burning and deforestation, which are partially the result of agricultural activity, are included in the Land-Use Module.

Land-Use and Natural Source Module

This module consists of components dealing with a number of land surface processes and other natural sources of trace gases. The most important of these is carbon dioxide released from land-

use change, particularly deforestation, which is projected with the Marine Biological Laboratory/Terrestrial Carbon Model (MBL/TCM; Houghton et al., 1983). Methane emissions from wetlands are projected based on the data set of Matthews and Fung (1987) and will incorporate temperature feedback. Emissions of CO, CH_4, N_2O, and NO_x from biomass burning, soils, and oceans are based on analysis of the literature, and generally are held constant throughout the projection period.

Ocean Module

Ocean uptake of CO_2 and heat are modeled using the Box-Diffusion approach introduced by Oeschger et al. (1975) as implemented for the GISS GCM (Hansen et al., 1984). Alternative ocean model formulations for CO_2, such as the Advective-Diffusive Model (Bjorkstrom, 1979), and the Outcrop-Diffusion Model (Siegenthaler, 1983) will be included in the integrating framework and can be used in the sensitivity analysis.

Atmospheric Composition Module

The Atmospheric composition model was developed for this study by Prather et al. and is currently being peer reviewed at NASA/GISS. It estimates changes in the concentration of key atmospheric constituents and the global radiation balance based on the emissions/uptake projected by the other modules. Perturbations to atmospheric chemistry are incorporated based on first-order (and occasionally second-order) relationships derived from more complex chemical models and observations. Global surface temperature change is calculated based on the radiative forcing of the greenhouse gases derived from Lacis et al. (1981) coupled to heat uptake by the ocean model using a specified climate sensitivity parameter.

Scenarios

This framework is not intended to predict the future, but rather to allow systematic assessments of the implications of various technological and economic choices and assumptions. While the absolute level of global warming in any given year depends on a large number of variables that can not be specified with any confidence, the relative impact of specific assumptions and policy options is much more robust. Thus we do not ask: How warm will the earth be in 2100? Rather we consider, for example, how important technical change in rice production could be in comparison to more efficient automobiles, in terms of the rate of global climate change that is realized during the next century.

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Atmospheric Stabilization Framework
Flow Diagram

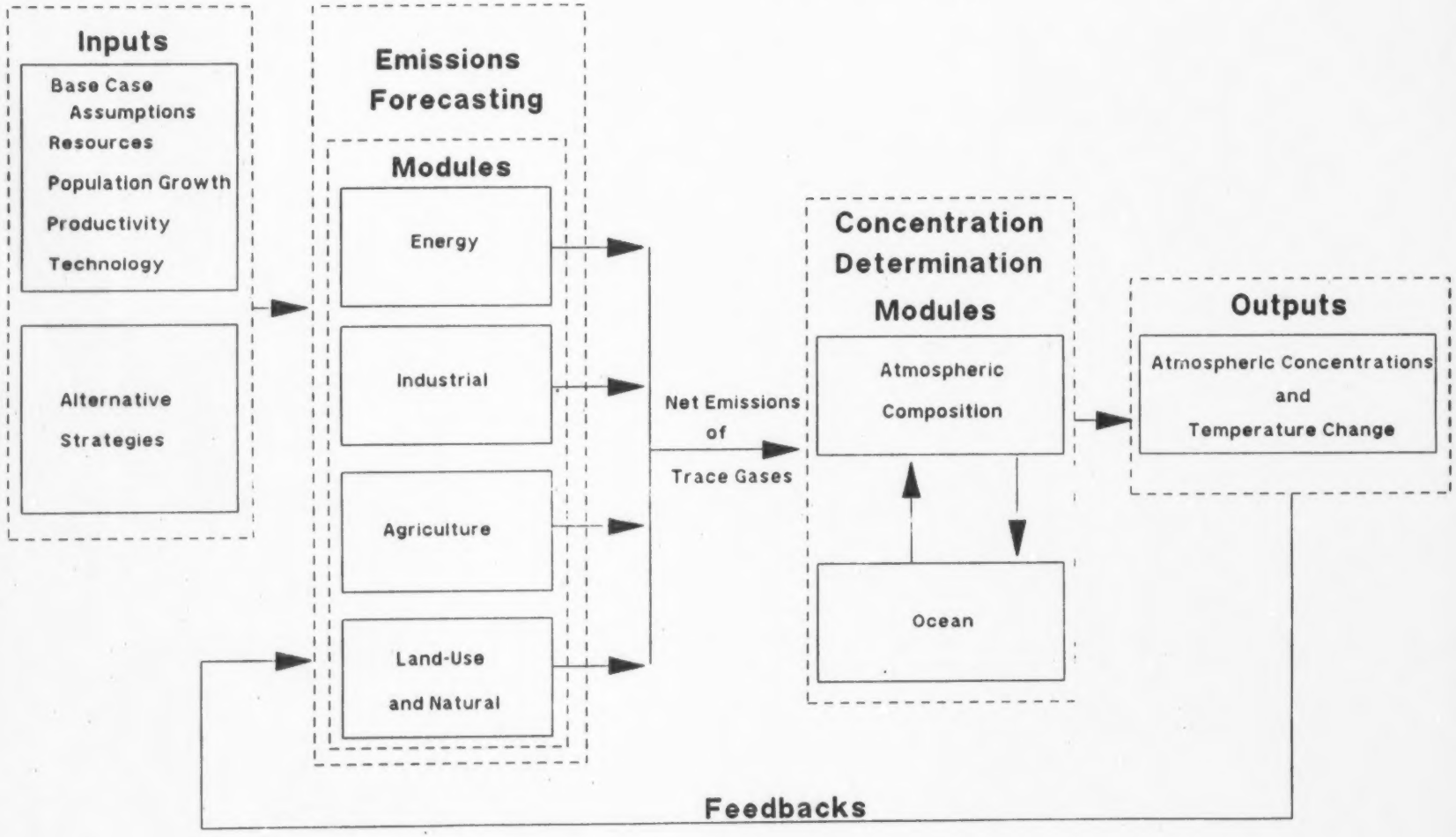

Figure A-1.

APPENDIX B

MEETING AGENDA

EPA/NOAA/NASA/USDA N_2O WORKSHOP
SEPTEMBER 15,16 1987
BOULDER, COLORADO

PLANNED AGENDA

Tuesday September 15, 1987

7:30 - 8:30	Registration, Name Tags, etc.	
8:30	Opening Comments	Steve Lanier
8:40	Overview of EPA Programs	Dennis Tirpak
9:10	Overview of NASA Programs	Mel Averner
9:30	Overview of NOAA Programs	Jim Elkins
9:45	Overview of USDA Programs	Gordon Hutchinson
10:00	Discussion of Program Format, Anticipated Workshop Outputs, General Announcements	David Mobley, Joe McSorley, and Gordon Hutchinson
10:30	Coffee Break	

11:00 Joint Discussion of N_2O Measurement Techniques
Hardware Development
Discussion Leader - Jim Elkins

Anticipated Key Participants:
TECO
Tami Montgomery/Larry Muzio
Jim Elkins
Mark Zahniser

11:45 Develop Workshop Position Statement on R&D Needs for N_2O Instrumentation

12:00 Lunch

1:00 Reconvene in Parallel Biogenic/Combustion Sessions

PLANNED AGENDA (CONTINUED)

Detailed agendas for the Combustion Source and Biogenic Source Sessions are detailed on the following sheets. Both sessions are divided into three major areas. Areas I and II will be discussed on Tuesday afternoon while area III will be the topic of discussion for Wednesday morning. Consistent with the desire for free and open discussion of the issues, no detailed time schedules are provided for either of the parallel sessions. It is anticipated that both groups can complete discussion of their respective topic area III by approximately 10:30 to 11:00 on Wednesday morning, at which time the two groups will reconvene in a joint wrap up session. Planned content for the joint wrap up session is detailed below.

Late Morning	Both Groups Reconvene for Wrap Up Session
	Summary Report from Each Session Leader
	Review of Degree to Which Program Goals were Achieved
	European Workshop Plans
	Closing Comments by Each Sponsoring Agency
	EPA
	NASA
	NOAA
	USDA
1:00 - 1:30	Adjourn

AGENDA FOR COMBUSTION SOURCE SESSION

Introduction - Overview and Focus of This Session, Critical Issues
Session Chairman - Steve Lanier

I. Discussion of Processes Controlling N_2O Emissions
Discussion Leader - Gerard deSoete

A. EPA N_2O Results
B. MIT/Harvard
C. Stanford
D. Lawrence Berkley Labs
E. UCI
F. Others (U of A, CRB, etc.)

II. Rates, Reactions and Mechanisms
Discussion Leader - C. Tom Bowman

A. Gas Phase Reactions
B. Coal Devolatilization
C. Heterogeneous Reactions

III. Research and Development Needs
Discussion Leader - Larry Muzio

A. Fundamental
B. Pilot
C. Field

AGENDA FOR BIOGENIC SOURCE SESSION

I. Contribution of Biogenic Sources to the Atmospheric N_2O Budget
Discussion Leader - Gordon Hutchinson

A. Measurement of Biogenic N_2O Emission for Individual Source Regions

1. Grass Lands	Schimer
2. Temperate Forests	Bowden
3. Tropical Forest	Keller/Livingston
4. Wetlands	Brosemer
5. Aquatic Ecosystems	Elkins
6. Agriculture	Brietenbeck
7. Fertilizers	Eichner/Pepper

B. Scaling Point Measurements to Characterize Source Regions

II. Biochemical Mechanisms for N_2O Production and Destruction
Discussion Leader - Mary Firestone

A. N_2O Production During Nitrification	Hooper
B. N_2O Production During Denitrification	Smith
C. N_2O Destruction at the Earth's Surface	Matson
D. Rate Controlling Factors in N_2O Production	Kohl/Mosier

III. Modeling the Dynamics of Atmospheric N_2O
Discussion Leader - Joel Levine

A. History of Changes in Atmospheric N_2O Concentration	Rasmussen
B. Comparison of Biogenic vs. Other N_2O Sources	Levine
C. NO vs. N_2O Production During Biological N Transformations	Hutchinson
D. Lessons from a Parallel Effort Concerning Atmospheric CH_4	Averner
E. Modelling N_2O Production from Agricultural Fertilizers	Fung

APPENDIX C

LIST OF ATTENDEES

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